

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE


In re Appellant:

CHARLES A. LIEDER
LLOYD E. FUNK
DAVID A. BARKER

Filed: April 21, 2000

Serial No.: 09/556,852

**For: GASOLINE-OXYGENATE BLEND
AND METHOD OF PRODUCING
THE SAME**



Group Art Unit: 1714

Examiner: C. Toomer

Attorney Docket No.: 013129-00025

APPEAL BRIEF

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AMENDED APPEAL BRIEF

MAIL STOP APPEAL BRIEF - PATENTS
 Commissioner for Patents
 P.O. Box 1450
 Alexandria, VA 22313-1450

Dear Sir:

In response to the Examiner's Office Action dated January 27, 2009, Appellants hereby submit this amended Appeal Brief. The requisite fee as set forth in 37 C.F.R. § 1.17(c) was provided on August 22, 2006 with the filing of the Appeal Brief . A Notice of Appeal was timely filed on August 16, 2006. Accordingly, this Appeal Brief is accordingly timely filed.

I. REAL PARTY IN INTEREST

The real party in interest in this appeal is Shell Oil Company, a corporation formed under the laws of the State of Delaware, to whom this application has been assigned.

II. RELATED APPEALS AND INTERFERENCES

No related appeals or interferences exist.

III. STATUS OF CLAIMS

As originally filed, this application contained Claims 1-29. Claims 1-40 are active in this application. The Examiner has rejected Claims 1-40 on the grounds discussed herein. Accordingly, the claims on appeal are Claims 1-40. A copy of the claims on appeal is set forth in the *Appendix*. Each of these claims stands finally rejected for which Appellants bring the present appeal to the Board.

IV. STATUS OF AMENDMENT

Claims 1, 10, 16-18, 23, and 26 were amended in the Amendment and Response to the Office Action Dated September 10, 2004. No amendments were made subsequent to the Final Rejection dated March 3, 2005. All amendments were made prior to the final rejection and have been entered into the record and considered by the Examiner.

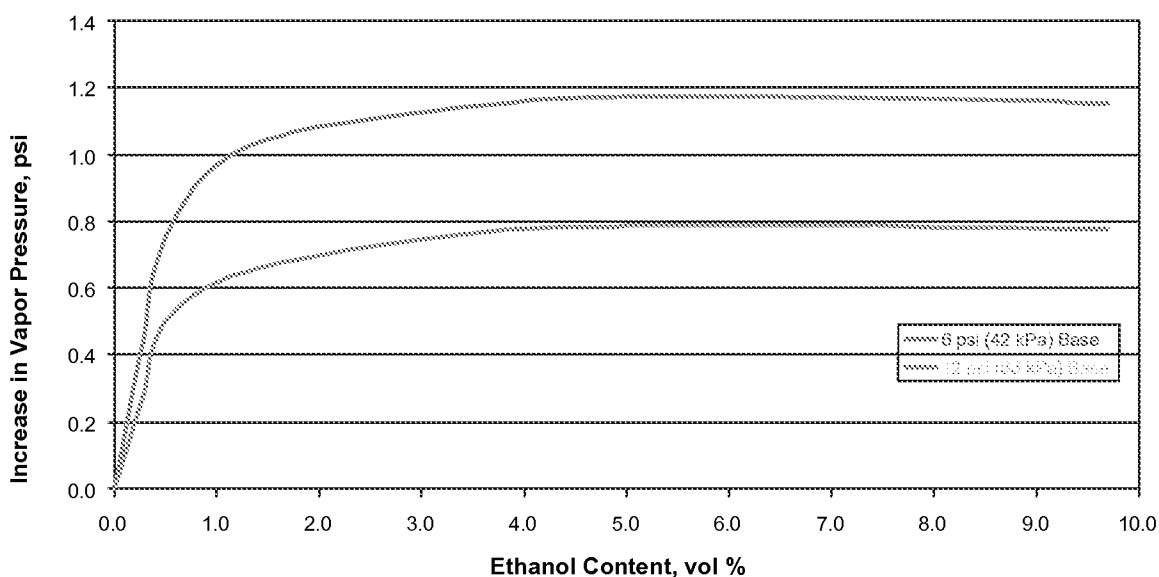
V. SUMMARY OF CLAIMED SUBJECT MATTER

Appellants' invention relates to novel gasoline-oxygenate blends suitable for use in automotive engines containing at least one alcohol. The relatively low boiling point of alcohols (e.g., the boiling point of ethanol is 78 °C), while being significantly higher than the initial boiling point of gasoline (approximately 30 °C), is lower than the mid-boiling point of gasoline

(approximately 100°C). The vapor pressure of neat alcohols is lower than that of gasoline. Consequently one would expect that blending an alcohol with gasoline would reduce the Reid Vapor Pressure (“RVP”) (defined in 11. 5-8, p. 7) and somewhat increase mid-range volatility. However, when alcohol is blended with gasoline at concentrations up to around 30%, there is an unexpected increase in vapor pressure which causes the blend to have significantly higher RVP than the base gasoline. This is shown in FIG. 1 below for ethanol:

FIG. 1

Effect of ethanol addition on Reid Vapor Pressure (RVP) at two levels of base fuel RVP



The effect of alcohols, such as methanol and ethanol, on the increase in vapor pressure of a gasoline blend is further reported in Chapter 2 of API Publication 4261, a copy of which was attached to the Amendment and Response to Office Action of June 4, 2002, filed on October 4, 2002. Note in particular Figs. 9, 10 and 11. As clearly shown in Figure 9, the maximum RVP increase occurs at around 5-15 % v/v alcohol. This is the level of alcohol in most commercial blends. The resulting blend is often too volatile, unless base fuel volatility is adjusted to meet

fuel specifications. Fig. 10 of API Publication 4261 further shows that the addition of 10 % v/v ethanol to a base fuel composition typically raises the RVP by about 1 PSI; the increase for 10% v/v methanol being almost 3 PSI.

Gasoline-oxygenate blends of gasoline formulations exhibiting the RVP and alcohol volume specifications recited in the claims of Appellants dramatically reduce (and in most instances, eliminate) the need for methyl t-butyl ether (MTBE) in gasoline formulations. In addition, the claimed gasoline-oxygenate blends provide increased percentile reductions of NO_x, toxic pollutants and VOCs. Compare, for instance, the data for Percent Reduction (“% Red”) in NO_xR, ToxR and VOCR in Table 9 for A2, C2, D2, E2, F2, I2, J2, L2, O2, Q2, R2 and S2 (outside of the claimed blends) versus A1, C1, D1, E1, F1, I1, J1, L1, O1, Q1, R1 and S1, respectively (within the claims of Appellants).

The novel compositions of Appellants meet RVP specifications *by adjustment to the base fuel composition*. Note, for instance, reference to the preferred butane percentile in the FFB (defined in ll. 26-27, p. 14 through l. 2, p. 15 of the specification). This, in turn, causes a reduction in the vapor pressure of the light components of the base gasoline. The addition of alcohol to the base gasoline renders a RVP within the claimed limitations. In one embodiment of the invention, the alcohol may be introduced to the base gasoline at a remote location, such as a distribution terminal. This is often necessary since gasoline containing an alcohol cannot generally be shipped via common pipelines.

The subject matter of the independent claims have been supported and defined as follows. Claim 1. A gasoline-oxygenate blend, suitable for combustion in an automotive engine, having the following properties: (a) a Dry Vapor Pressure Equivalent less than about 7.2 PSI (supported in part by *Application*, p. 22, l. 1-p. 23, l. 2, Table 9 and p. 28, l. 3-7, Table 14); and (b) an

alcohol content which is greater than about 5.0 volume percent but less than or equal to 10 volume percent (supported in part by *Application*, pp. 20, l. 1-p. 21, l. 2, Table 8 and p. 27, l. 10-12, Table 13). Claim 10. A gasoline-oxygenate blend, suitable for combustion in an automotive engine, comprising at least two hydrocarbon streams and an oxygenate stream consisting essentially of an alcohol and having: a Dry Vapor Pressure Equivalent less than about 7.2 PSI (supported in part by *Application*, p. 22, l. 1-p. 23, l. 2, Table 9 and p. 28, l. 3-7, Table 14); and an alcohol content greater than about 5.0 volume percent (supported in part by *Application*, pp. 20, l. 1-p. 21, l. 2, Table 8 and p. 27, l. 10-12, Table 13). Claim 18. A gasoline-oxygenate blend, suitable for combustion in an automotive engine having the following properties: (a) a Dry Vapor Pressure Equivalent less than about 7.2 PSI (supported in part by *Application*, p. 22, l. 1-p. 23, l. 2, Table 9 and p. 28, l. 3-7, Table 14); and (b) an alcohol content greater than about 5.0 volume percent (supported in part by *Application*, pp. 20, l. 1-p. 21, l. 2, Table 8 and p. 27, l. 10-12, Table 13) wherein the benzene content of the blend is greater than 0.27 volume percent (supported in part by *Application*, pp. 24, l. 6-25, l. 3, Table 10). Claim 23. A process for preparing a gasoline-oxygenate blend comprising combining a blend of hydrocarbons with a stream consisting essentially of an alcohol, wherein the resulting gasoline-oxygenate blend has the following properties: (a) a Dry Vapor Pressure Equivalent less than about 7.2 PSI (supported in part by *Application*, p. 22, l. 1-p. 23, l. 2, Table 9 and p. 28, l. 3-7, Table 14); and (b) an alcohol content greater than about 5.0 volume percent (supported in part by *Application*, pp. 20, l. 1-p. 21, l. 2, Table 8 and p. 27, l. 10-12, Table 13). Claim 26. A process for preparing a gasoline-oxygenate blend comprising combining a blend of hydrocarbons with an alcohol, wherein the resulting gasoline-oxygenate blend has a Dry Vapor Pressure Equivalent less than about 7.2 PSI (supported in part by *Application*, p. 22, l. 1-p. 23, l. 2, Table 9 and p. 28, l. 3-7,

Table 14); and an alcohol content less than or equal to 10 volume percent (supported in part by *Application*, p. 20, l. 1-p. 21, l. 2, Table 8 and p. 27, l. 10-12, Table 13). Claim 30. A gasoline-oxygenate blend, suitable for combustion in an automotive engine having the following properties: (a) a Dry Vapor Pressure Equivalent less than about 7.2 PSI (supported in part by *Application*, p. 22, l. 1-p. 23, l. 2, Table 9 and p. 28, l. 3-7, Table 14); and (b) an alcohol content greater than about 5.0 volume percent (supported in part by *Application*, pp. 20, l. 1-p. 21, l. 2, Table 8 and p. 27, l. 10-12, Table 13) wherein the aromatic content of the blend is greater than 16.76 volume percent (supported in part by *Application*, p. 24, l. 6-p. 25, l. 3, Table 10). Claim 34. A gasoline-oxygenate blend, suitable for combustion in an automotive engine having the following properties: (a) a Dry Vapor Pressure Equivalent less than about 7.2 PSI (supported in part by *Application*, p. 22, l. 1-p. 23, l. 2, Table 9 and p. 28, l. 3-7, Table 14); and (b) an alcohol content greater than about 5.0 volume percent (supported in part by *Application*, pp. 20, l. 1-p. 21, l. 2, Table 8 and p. 27, l. 10-12, Table 13) wherein the olefin content of the blend is greater than 1.15 volume percent (supported in part by *Application*, p. 24, l. 6-p. 25, l. 3, Table 10). Claim 38. A process for preparing a gasoline-oxygenate blend which comprises adjusting a hydrocarbon base fuel having a Dry Vapor Pressure Equivalent greater than or equal to 5.3 PSI with an alcohol (supported in part by *Application*, p. 26, ll. 6-8, Table 12), wherein the Dry Vapor Pressure Equivalent of the gasoline-oxygenate blend is not greater than 7.2 PSI (supported in part by *Application*, p. 22, l. 1-p. 23, l. 2, Table 9 and p. 28, l. 3-7, Table 14); and further wherein the alcohol content of the gasoline-oxygenate blend is greater than about 5.0 volume percent (supported in part by *Application*, pp. 20, l. 1-p. 21, l. 2, Table 8 and p. 27, l. 10-12, Table 13).

VI. GROUND OF REJECTION TO BE REVIEWED ON APPEAL

The issues on appeal are premised on the grounds of rejection set forth on pages 2-4 of the Final Office Action dated March 8, 2005 and reiterated in the Final Office Action dated May 17, 2006. The issues are as follows:

1. Whether Claims 1, 17, 18, 26, 30, 34, 38 and their dependents fail are unpatentable under 35 U.S.C. § 112, First Paragraph, for failing to comply with the written description requirement.
2. Whether Claims 1, 4-10, 13-18, and 21-29 are unpatentable under 35 U.S.C. § 102(b) over U.S. Patent No. 5,679,117 (“*Jarvis*”).
3. Whether Claims 11-12 are allowable.

VII. ARGUMENT

A. The Examiner Has Improperly Maintained the Rejection of Claims 1, 17, 18, 26, 30, 34, 38 and their dependents under 35 U.S.C. § 112, First Paragraph.

The Examiner has maintained a rejection of Claims 1, 17, 18, 26, 30, 34, 38 and their dependents under 35 U.S.C. § 112, First Paragraph as failing to comply with the written description requirement. The following presents each of the contentions of the Examiner and the written support from the Application as filed for the Claims. In order to comply with the written description requirement, the specification “need not describe the claimed subject matter in exactly the same terms as used in the claims; it must simply indicate to persons skilled in the art that as of the [filing] date the applicant had invented what is now claimed.” *E.g., Eiselstein v. Frank*, 52 F.3d 1035, 1038, 34 U.S.P.Q.2d 1467, 1470 (Fed. Cir. 1995) (citing *Vas-Cath Inc. v. Mahurkar*, 935 F.2d 1555, 1562, 19 U.S.P.Q.2d 1111, 1115 (Fed. Cir. 1991) and *In re Wertheim*, 541 F.2d 257, 265, 191 U.S.P.Q. 90, 98 (C.C.P.A. 1976)). “The test for determining compliance with the written description requirement is whether the disclosure of the application as originally

filed reasonably conveys to the artisan that the inventor had possession at that time of the later claimed subject matter, rather than the presence or absence of literal support in the specification for the claim language.” *In re Kaslow*, 707 F.2d 1366, 1375, 217 U.S.P.Q. 1089, 1096 (Fed. Cir. 1983). As illustrated below, the Application as filed supported the current Claims.

1. Rejection of Claims 1, 17, and 26.

The Examiner rejected Claims 1, 17, and 26 for the inclusion of “less than or equal to 10 volume percent.” Appellants respectfully note that the Specification as filed contained Table 8: Phase I Gasoline-Oxygenate Blend Recipes, that is reprinted herein, which provided support for this element:

TABLE 8: PHASE I GASOLINE-OXYGENATE BLEND RECIPES

BLEND	EtOH	C4	FFB	RAFF	HOR	TOL	LCC	ALKY	LSCC	HCC
	(in terms of volume percent of the total blend) (%)									
A1	9.50	0.00	1.27	0.00	20.72	17.92	8.05	42.54	0.00	0.00
A2	5.42	0.0	1.3	0.0	21.7	18.7	8.4	44.5	0.0	0.0
B2	9.50	0.00	0.00	15.39	16.20	9.41	0.00	23.89	10.59	15.02
B2	5.42	0.0	0.0	16.1	16.9	9.8	0.0	25.0	11.1	15.7
C1	9.50	1.45	0.00	0.00	14.93	27.60	13.39	33.12	0.00	0.00
C2	5.42	1.5	0.0	0.0	15.6	28.8	14.0	34.6	0.0	0.0
D1	9.50	0	0	15.7	24.8	0	12.8	15.7	18.6	2.9
D2	5.42	0.0	0.0	16.5	25.9	0.0	13.3	16.5	19.4	3.0
E1	9.50	0.00	0.00	22.63	25.25	0.00	0.00	15.84	16.83	9.86
E2	5.42	0.0	0.0	23.6	26.4	0.0	0.0	16.6	17.6	10.3
F1	9.50	0.00	0.00	9.14	9.23	32.85	16.47	22.81	0.00	0.00
F2	5.42	0.0	0.0	9.6	9.6	34.3	17.2	23.8	0.0	0.0
G1	9.50	0.09	3.35	0.00	34.39	7.15	9.50	35.93	0.00	0.00
G2	5.42	0.1	3.5	0.0	35.9	7.5	9.9	37.5	0.0	0.0
H	9.50	0.00	0.00	12.49	15.48	0.00	0.09	25.61	18.55	18.19
I1	9.50	0.00	1.81	19.10	8.78	19.28	11.31	9.68	20.54	0.00
I2	5.42	0.0	1.9	20.0	9.2	20.1	11.8	10.1	21.5	0.0
J1	9.50	0.00	1.45	0.00	31.77	9.59	12.94	32.67	0.00	2.08
J2	5.42	0.0	1.5	0.0	33.2	10.0	13.5	34.1	0.0	2.2
K1	9.50	0.00	0.00	20.27	17.47	13.39	7.24	20.72	10.05	1.36
K2	5.42	0.0	0.0	21.2	18.3	14.0	7.6	21.7	10.5	1.4
L1	9.40	0.00	0.00	23.47	16.13	7.34	13.32	10.87	17.03	2.54
L2	5.42	0.0	0.0	24.5	16.8	7.7	13.9	11.3	17.8	2.6
M	9.50	0.00	0.00	11.67	19.10	0.18	9.96	20.27	17.20	12.13

BLEND	EtOH	C4	FFB	RAFF	HOR	TOL	LCC	ALKY	LSCC	HCC
	(in terms of volume percent of the total blend) (%)									
N	9.72	0.00	0.72	18.33	4.15	23.20	17.42	0.00	17.33	9.21
O1	9.79	0.00	2.71	0.00	20.57	15.97	9.11	36.26	0.00	5.68
O2	5.42	0.0	2.8	0.0	21.6	16.7	9.6	38.0	0.0	6.0
P	9.72	0.00	0.00	15.98	0.00	19.23	6.68	19.41	15.80	13.27
Q1	9.64	0.00	0.00	17.80	4.70	14.64	3.34	12.83	18.61	18.52
Q2	5.42	0.0	0.0	18.6	4.9	15.3	3.5	13.4	19.5	19.4
R1	9.59	0.00	0.00	20.52	17.36	5.33	7.23	5.79	23.87	10.22
R2	5.42	0.0	0.0	21.5	18.2	5.6	7.6	6.1	25.0	10.7
S1	9.69	0.00	0.99	11.56	0.00	26.55	14.54	36.76	0.00	0.00
S2	5.42	0.0	1.0	12.1	0.0	27.8	15.2	38.5	0.0	0.0
T	9.66	0	0	13.5	15.3	4.2	15.4	12.3	26.6	3.3
U	9.66	0	0	4.2	12.8	15.7	7.5	32.2	0	17.9
V	9.81	0	0	19.1	13.3	0	0	17.2	26.8	13.7
W	9.67	0	0	0	32	11.8	26.7	19.7	0	0
X	9.65	0	0	9.7	0	0.4	0.73	34.5	24	21.1

Application, pp. 20-21. These blends show “an alcohol content which is greater than about 5.0 volume percent but less than or equal to 10 volume percent” as labeled EtOH column in this example. As shown, the EtOH or alcohol content of samples A1-X contain an alcohol content which is greater than about 5.0 volume percent but less than or equal to 10 volume percent.

Similarly, Appellants respectfully note that the Specification as filed contained Table 13: Phase II Gasoline-Oxygenate Blend Recipes, that is reprinted herein:

TABLE 13: PHASE II GASOLINE-OXYGENATE BLEND RECIPES

BLEND	EtOH	C4	FFB	RAFF	HOR	TOL	LCC	ALKY	LSCC	HCC
	(in terms of volume percent of the total blend) (%)									
AA	9.750	0.0	4.1	13.3	14.0	24.0	0.0	34.9	0.0	0.0
BB	9.900	0.0	0.0	18.2	17.6	0.0	18.7	13.7	19.7	2.3
CC	9.680	0.0	0.0	16.4	30.3	0.2	0.0	24.6	1.4	17.3
DD1	9.610	0.0	1.5	0.1	11.6	16.5	19.6	35.2	6.1	0.0
DD2	5.420	0.0	1.6	0.1	12.1	17.2	20.5	36.8	6.3	0.0
EE1	9.450	0.0	0.2	2.2	2.1	24.8	22.9	36.6	1.8	0.0
EE2	5.420	0.0	0.2	2.3	2.2	25.9	23.9	38.2	1.9	0.0
FF	9.640	0.4	0.0	20.6	30.5	0.0	1.5	16.0	8.0	13.4
GG	9.560	0.0	4.4	6.4	15.7	35.2	16.4	12.3	0.0	0.0
HH	9.910	0.8	0.2	21.2	36.7	0.2	4.1	4.8	13.2	8.9
II	9.760	0.0	2.0	2.9	34.9	12.4	15.2	21.7	0.0	1.3
JJ	9.660	0.0	0.0	25.2	0.1	18.6	15.0	12.3	19.2	0.0
KK1	9.620	0.0	0.6	5.3	4.2	28.6	20.2	31.6	0.0	0.0
KK2	5.420	0.0	0.7	5.6	4.4	29.9	21.1	33.1	0.0	0.0

Application, p. 27. These blends show “an alcohol content which is greater than about 5.0 volume percent but less than or equal to 10 volume percent” as labeled EtOH column in this example. As shown, the EtOH or alcohol content of samples AA-KK2 contain an alcohol content which is greater than about 5.0 volume percent but less than or equal to 10 volume percent.

Accordingly, there is support for the limitation of this range in Claims 1, 17, 26, and their dependencies. The tables include sufficient data regarding the alcohol content to show that the Appellants were in possession of the invention.

2. Rejection of Claim 18.

With respect to the requirement of a “benzene content of the blend is greater than 0.27 volume percent” in Claim 18 and its dependencies, the Appellants note that in Table 10: Additional Phase I Gasoline-Oxygenate Blend Properties, Blend X contains a 0.27 Volume Percent Benzene. The Table from the specification is reprinted below:

TABLE 10: ADDITIONAL PHASE I GASOLINE-OXYGENATE BLEND PROPERTIES

Blend	Oxy	Benz	Sulfur	Olef	Arom	NOxR	ToxR	VOCR
	Wt%	Vol%	PPMW	Vol%	Vol%	% Red	% Red	% Red
A1	3.54	0.53	23	1.41	23.25	15.7	40.4	47.5
A2	2.02	0.55	24	1.47	24.30	15.8	39.5	43.9
B1	3.49	0.58	197	2.90	25.01	7.2	34.5	39.5
B2	1.99	0.61	206	3.03	26.14	7.1	33.1	35.9
C1	3.47	0.53	34	2.31	33.89	13.5	35.2	44.6
C2	1.98	0.55	36	2.41	35.41	13.1	32.7	37.8
D1	3.56	0.71	80	3.68	23.75	12.1	33.4	33.8
D2	2.03	0.75	84	3.85	24.83	12.0	32.8	31.1
E1	3.58	0.68	143	1.92	24.34	9.3	33.2	37.4
E2	2.04	0.71	149	2.01	25.43	9.4	32.6	37.2
F1	3.48	0.63	70	4.61	32.97	11.4	34.3	45.6
F2	1.99	0.66	73	4.82	34.46	11.7	32.3	45.6
G1	3.46	0.67	36	2.10	25.73	14.1	36	39.8
G2	1.97	0.70	38	2.20	26.89	14.4	35.4	41.3
H	3.55	0.52	261	4.30	16.76	7.5	36.8	39.3
I1	3.52	0.70	68	3.08	31.08	11.5	32.1	37.8
I2	2.01	0.73	71	3.21	32.48	11.6	30.9	36.1
J1	3.53	0.85	83	3.79	28.20	11.5	31.8	41.7
J2	2.01	0.89	87	3.96	29.47	11.6	29.9	39.0
K1	3.54	1.05	106	2.38	24.83	10.5	29.9	36.6
K2	2.02	1.10	111	2.49	25.95	10.6	29.3	40.4
L1	3.45	0.69	108	2.82	27.83	9.9	33.6	39.9
L2	1.99	0.72	113	2.94	29.06	9.7	32.7	38.2
M	3.50	0.77	215	4.70	26.14	6	30.3	37.6
N	3.51	0.78	247	7.39	31.62	3.2	27.1	35.6
O1	3.59	0.64	116	3.99	28.50	9.9	33.8	37.5
O2	1.99	0.67	122	4.18	29.88	9.8	32.4	36.4
P	3.56	0.51	213	3.06	25.15	6.2	35.8	38.3
Q1	3.50	0.69	260	1.15	30.83	3.9	28.2	36.7
Q2	1.97	0.73	272	1.21	32.27	3.7	26.3	33.6
R1	3.54	0.85	177	4.55	27.11	7.1	28.8	33.3
R2	2.00	0.89	185	4.76	28.36	7.1	27.5	32.6
S1	3.59	0.56	88	4.20	23.60	11.8	39.1	38.7
S2	2.01	0.59	92	4.40	24.71	11.8	37.7	36.5
T	3.54	0.73	128	2.11	28.15	9.3	31.4	38.3
U	3.54	0.49	250	4.86	25.18	5.3	35.3	39.2
V	3.61	0.64	177	3.32	22.57	8.4	34.1	37.4
W	3.50	0.81	110	5.41	33.39	9.1	29.9	38.3

Blend	Oxy	Benz	Sulfur	Olef	Arom	NOxR	ToxR	VOCR
	Wt%	Vol%	PPMW	Vol%	Vol%	% Red	% Red	% Red
X	3.58	0.27	286	5.92	32.65	2.7	32.4	35.2

Application, pp. 24-25. Accordingly, there is support for the limitation of this range in Claim 18 and its dependencies. The table includes sufficient data to show that the Appellants were in possession of the invention and provided a written description of same; accordingly reconsideration is respectfully requested.

3. Rejection of Claim 30.

With respect to the requirement of a “the aromatic content of the blend is greater than 16.76 volume percent” in Claim 30 and its dependencies, Appellants note that in Table 10: Additional Phase I Gasoline-Oxygenate Blend Properties, Blend H contains an aromatic content of the blend of 16.76 volume percent is disclosed. The Table was reprinted above.

Accordingly, there is support for the limitation of this range in Claim 30 and its dependencies. The table includes sufficient data to show that the Appellants were in possession of the invention and provided an adequate description.

4. Rejection of Claim 34.

With respect to the requirement of “the olefin content of the blend is greater than 1.15 volume percent” in Claim 34 and its dependencies, the Appellants note that in Table 10: Additional Phase I Gasoline-Oxygenate Blend Properties, Blend Q1 contains an olefin content of 1.15 volume percent. The Table was reprinted above.

Accordingly, there is support for the limitation of this range in Claim 34 and its dependencies. The table includes sufficient data to show that the Appellants were in possession of the invention.

5. Rejection of Claim 38.

With respect to the requirement of “a Dry Vapor Pressure Equivalent greater than or equal to 5.3 PSI” in Claim 38 and its dependencies, the Appellants note that in Table 12: Phase II Neat Blend Recipes Properties, Blends BB and CC contain a Dry Vapor Pressure Equivalent of 5.3 PSI. This limitation is also disclosed. The Table is reprinted below.

TABLE 12: PHASE II NEAT BLEND RECIPES PROPERTIES

Blend	RON	MON	(R+M)/2	DVPE	T10	T50	T90	EP	E200	E300
				PSI	°F	°F	°F	°F	Vol. %	Vol. %
AA	96.5	87.5	92.0	5.5	156.3	224.5	308.5	387.0	30.5	88.0
BB	88.1	81.9	85.0	5.3	145.4	213.7	342.0	415.5	42.9	79.1
CC	90.7	83.6	87.2	5.3	150.6	214.7	327.7	406.2	40.0	83.1
DD	96.3	87.7	92.0	5.5	151.4	222.6	308.3	398.3	33.1	88.1
EE	96.6	87.9	92.3	5.5	159.0	217.1	277.0	375.7	33.9	92.1
FF	89.8	82.5	86.2	5.5	145.9	218.4	336.0	414.6	40.2	79.9
GG	97.2	86.8	92.0	5.5	153.8	228.1	303.9	386.3	29.9	88.8
HH	89.0	81.8	85.4	5.5	146.3	231.5	340.8	416.3	36.9	75.1
II	96.4	87.2	91.8	5.5	152.7	231.4	323.4	393.0	30.3	83.2
JJ	88.4	81.9	85.2	5.4	150.1	213.0	322.6	414.5	41.1	85.4
KK	96.6	87.0	91.8	5.4	159.9	218.4	281.2	374.0	32.8	92.1

Application, p. 26.

Accordingly, support for the limitation of this range in Claim 38 and its dependencies is present in the specification. The table includes sufficient data to show that the Appellants were in possession of the invention and disclosed same. The written description requirement is supported by the data provided in the Specification as filed. Accordingly, the grounds of rejection over the written requirement should be reversed.

B. The Examiner Has Improperly Maintained the Rejection of Claims 1, 4-10, 13-18, and 21-29 Under 35 U.S.C. §102(b) Over *Jarvis*.

The Examiner has rejected Claims 1, 4-10, 13-18, and 21-29 under 35 U.S.C. § 102(b) as being anticipated by *Jarvis*. To anticipate a claim, a reference must disclose every limitation of the claimed invention either explicitly or inherently. *In re Schreiber*, 44 U.S.P.Q.2d 1429, 1431 (Fed. Cir. 1997).

Jarvis does not disclose the alcohol content of the “final product.” Though a contestable RVP is listed for this final product, all of the rejected claims also recite an alcohol content. Claim 1 recites “an alcohol content which is greater than about 5.0 volume percent but less than or equal to 10 volume percent.” Claim 26 recites “an alcohol content less than or equal to 10 volume percent.” Claims 10 and 23 recite “an alcohol content greater than about 5.0 volume percent.” *Jarvis* fails to provide disclosure of an alcohol content of the “final product.”

Moreover, *Jarvis* fails to disclose a *blend* of gasoline and oxygenate. *Jarvis* discloses a reaction product, not a blend, of gasoline and an oxygenate. Each of Claims 1, 4-10, 13-17, and 23-29 specifically recite a gasoline-oxygenate blend. Appellants provided Declaration of Charles A. Lieder, Ph.D., under 37 C.F.R. § 1.132, submitted with Response to Office Action of February 10, 2003, filed on April 9, 2003, which established that *Jarvis* was directed to a chemical reaction and not a blend. The Examiner has failed to address the conclusions reached by Dr. Lieder that *Jarvis* is drawn to a reaction product because *Jarvis*:

- (1) discloses the use of a platinum catalyst in “an elongated catalyzing chamber” (lines 25-27 of column 1 of *Jarvis*). Catalysts are used to accelerate chemical reactions and are not useful in blends of mixtures;
- (2) characterizes his product as being derived from a “catalyzed mixture”;

(3) demonstrates a disparity in the reported physical properties of the products and the theoretical physical properties of the products (discussed below); and

(4) recites conditions characteristic of chemical reactions, as set forth in l. 25, col. 4 through l. 3., col. 5. *See* further paragraph 6 of Declaration of Dr. Lieder.

Because *Jarvis* fails to disclose a *blend* of gasoline and oxygenate and because each of Claims 1, 4-10, 13-17, and 23-29 recite an alcohol content that is not disclosed by the “final product” of *Jarvis*, the grounds of rejection over *Jarvis* should be reversed.

Even if independent Claims 1, 18, 23 and 26 and dependent claims 4, 7-9, 13, 15-17, 21-22, 24-25 and 27-29 are anticipated by *Jarvis*, which they are not, Claims 5-6 and 14 are not anticipated by *Jarvis* because *Jarvis* does not address the need for reducing toxic air pollutants emissions, much less provide a percentile amount for the reduction in toxic air pollutant emissions by the use of the disclosed hydrocarbons. Thus, Claims 5-6 and 14 are not anticipated by *Jarvis*.

Further, the Examiner has not argued that the rejection of Claims 5-6 and 14 is based on inherency and cannot now meet such a burden. *Ex parte Levy*, 17 U.S.P.Q.2d 1461, 1464 (Bd. Pat. App. & Int. 1990) (the Examiner must show “a basis in fact and/or technical reasoning to reasonably support the determination that the allegedly inherent characteristic necessarily flows from the teachings of the applied prior art.”).

C. Claims 11 and 12 are Allowable.

In the September 10, 2004 Non-Final Office Action, the Examiner rejected Claims 1-29 as begin unpatentable in view of U.S. Patent No. 5,697,987 (“Paul”). The only rejections to Claims 11 and 12 were related to *Paul*. The March 8, 2005 Final Office Action withdrew the use of *Paul* as a reference against the claims. Accordingly, Appellants respectfully submit that Claims 11 and 12 are allowable as no rejection is currently pending against these claims.

VIII. CONCLUSION

The rejections of:

- Claims 1-9, 17-22, 26-40 under 35 U.S.C. § 112, First Paragraph; and
- Claims 1, 4-10, 13-18, and 21-29 under 35 U.S.C. § 102(b) over *Jarvis*
- Claims 11 and 12 over *Paul*

are improper for the reasons discussed herein. Accordingly, Claims 1-40 are in condition for allowance and the rejections of the Examiner should be REVERSED.

A decision of the Board consistent with this showing is earnestly requested.

Respectfully submitted,

Date: February 26, 2009

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IX. CLAIMS APPENDIX

1. A gasoline-oxygenate blend, suitable for combustion in an automotive engine, having the following properties:
 - (a) a Dry Vapor Pressure Equivalent less than about 7.2 PSI; and
 - (b) an alcohol content which is greater than about 5.0 volume percent but less than or equal to 10 volume percent.
2. The blend of Claim 1 wherein the blend has a 50% distillation point less than about 195°F.
3. The blend of Claim 1 wherein the blend has a 10% distillation point less than about 126°F.
4. The blend of Claim 1 wherein the blend has an anti-knock index greater than or equal to about 89.
5. The blend of Claim 1 wherein the blend is capable of reducing toxic air pollutants emissions by more than about 21.5%.
6. The blend of Claim 5 wherein the blend is capable of reducing toxic air pollutants emissions by more than about 30%.
7. The blend of Claim 1 wherein the blend has an oxygen weight percent that is greater than about 1.8 weight percent.
8. The blend of Claim 1 wherein the blend contains ethanol.
9. The blend of Claim 1 wherein the blend contains essentially no methyl t-butyl ether.

10. A gasoline-oxygenate blend, suitable for combustion in an automotive engine, comprising at least two hydrocarbon streams and an oxygenate stream consisting essentially of an alcohol and having:
 - a Dry Vapor Pressure Equivalent less than about 7.2 PSI; and
 - an alcohol content greater than about 5.0 volume percent.
11. The blend of Claim 10 wherein the blend has a 50% distillation point less than about 178°F.
12. The blend of Claim 10 wherein the blend has a 10% distillation point less than about 123°F.
13. The blend of Claim 10 wherein the blend has an anti-knock index greater than about 89.
14. The blend of Claim 10 wherein the blend is capable of reducing toxic air pollutants emissions by more than about 21.5%.
15. The blend of Claim 10 wherein the blend has an oxygen weight percent that is greater than about 1.8 weight percent.
16. The blend of Claim 10 wherein the oxygenate stream contains ethanol.
17. The blend of Claim 10 wherein the blend contains less than or equal to 10 volume percent of alcohol.
18. A gasoline-oxygenate blend, suitable for combustion in an automotive engine having the following properties:
 - (a) a Dry Vapor Pressure Equivalent less than about 7.2 PSI; and
 - (b) an alcohol content greater than about 5.0 volume percentwherein the benzene content of the blend is greater than 0.27 volume percent.

19. The blend of Claim 18 wherein the blend has a 50% distillation point less than about 250°F.
20. The blend of Claim 18 wherein the blend has a 10% distillation point less than about 158°F.
21. The blend of Claim 18 wherein the blend contains ethanol.
22. The blend of Claim 18 wherein the blend contains essentially no methyl t-butyl ether.
23. A process for preparing a gasoline-oxygenate blend comprising combining a blend of hydrocarbons with a stream consisting essentially of an alcohol, wherein the resulting gasoline-oxygenate blend has the following properties:
 - (a) a Dry Vapor Pressure Equivalent less than about 7.2 PSI; and
 - (b) an alcohol content greater than about 5.0 volume percent.
24. The process of Claim 23 wherein the alcohol is ethanol.
25. The process of Claim 23 wherein the resulting blend contains essentially no methyl t-butyl ether.
26. A process for preparing a gasoline-oxygenate blend comprising combining a blend of hydrocarbons with an alcohol, wherein the resulting gasoline-oxygenate blend has a Dry Vapor Pressure Equivalent less than about 7.2 PSI; and an alcohol content less than or equal to 10 volume percent.
27. The process of Claim 26 wherein the alcohol is ethanol.
28. The process of Claim 26 further comprising introducing ethanol during the blending.
29. The process of Claim 26 wherein the resulting gasoline-oxygenate blend contains essentially no methyl t-butyl ether.

30. A gasoline-oxygenate blend, suitable for combustion in an automotive engine having the following properties:
- (a) a Dry Vapor Pressure Equivalent less than about 7.2 PSI; and
 - (b) an alcohol content greater than about 5.0 volume percent
- wherein the aromatic content of the blend is greater than 16.76 volume percent.
31. The blend of Claim 30 wherein the blend has a 50% distillation point less than about 250°F.
32. The blend of Claim 30 wherein the blend has a 10% distillation point less than about 158°F.
33. The blend of Claim 30 wherein the blend contains ethanol.
34. A gasoline-oxygenate blend, suitable for combustion in an automotive engine having the following properties:
- (a) a Dry Vapor Pressure Equivalent less than about 7.2 PSI; and
 - (b) an alcohol content greater than about 5.0 volume percent
- wherein the olefin content of the blend is greater than 1.15 volume percent.
35. The blend of Claim 34 wherein the blend has a 50% distillation point less than about 250°F.
36. The blend of Claim 34 wherein the blend has a 10% distillation point less than about 158°F.
37. The blend of Claim 34 wherein the blend contains ethanol.
38. A process for preparing a gasoline-oxygenate blend which comprises adjusting a hydrocarbon base fuel having a Dry Vapor Pressure Equivalent greater than or equal to 5.3 PSI with an alcohol, wherein the Dry Vapor Pressure Equivalent of the gasoline-

oxygenate blend is not greater than 7.2 PSI and further wherein the alcohol content of the gasoline-oxygenate blend is greater than about 5.0 volume percent.

39. The process of Claim 38 wherein the alcohol is ethanol.
40. The process of Claim 38 wherein the resulting gasoline-oxygenate blend contains essentially no methyl t-butyl ether.

X. EVIDENCE APPENDIX

In compliance with 37 C.F.R. § 41.37, paragraph c(1)(ix), there are enclosed the following copies of evidence previously entered into the record by the Appellants and/or the Examiner, and relied upon herein. These copies of evidence are attached at the end of this Appeal Brief as EXHIBITs 1, 2, 3, and 4, wherein:

- EXHIBIT 1 is Chapter 2 of API Publication No. 4261, which was originally attached to the Amendment in Response to Office Action of June 4, 2002, filed October 4, 2002, and referenced within the present Appeal Brief on page 4;
- EXHIBIT 2 is U.S. Patent No. 5,679,117 to Jarvis, *et al.*, originally disclosed by Appellants in the Supplemental Information Disclosure Statement filed April 3, 2001, cited by the Examiner in the Office Action mailed June 4, 2002, and referenced within the present Appeal Brief on pages 13-14;
- EXHIBIT 3 is the Declaration of Charles A. Lieder, Ph.D. (and the associated Exhibits A and B) under 37 C.F.R. § 1.132, submitted with the Response to Office Action of September 10, 2004, filed on December 13, 2004, and referenced within the present Appeal Brief on pages 13-14; and

- EXHIBIT 4 is U.S. Patent No. 5,697,987 to *Paul*, originally cited by the Examiner in the September 10, 2004 Office Action, and referenced within the present Appeal Brief on page 16.

XI. RELATED PROCEEDINGS APPENDIX

None.

EXHIBIT 1

Alcohols and Ethers

A Technical Assessment of Their Application as Fuels and Fuel Components

Refining Department

**API PUBLICATION 4261
SECOND EDITION, JULY 1988**

**American
Petroleum
Institute**



Alcohols and Ethers — A Technical Assessment of Their Application as Fuels and Fuel Components

CHAPTER 1—INTRODUCTION AND SCOPE

In 1971 the American Petroleum Institute (API) studied the feasibility of blending ethanol with gasoline to augment domestic fuel supplies for transportation.¹ After the first Arab oil embargo in 1974 interest in using alcohols as fuels expanded to include methanol, not only as a transportation fuel but also as fuel for stationary power sources. In response to that expanded interest the API published an updated technical assessment in 1976.²

Since 1976 many changes have occurred in the use of non-petroleum fuels, both neat and in blends with hydrocarbon components. Today the earlier objective of augmenting domestic energy sources has been joined by two newer objectives: a) to produce high octane gasoline without the use of lead alkyls, and b) to reduce the contribution of motor vehicles and stationary sources to air pollution.

The Clean Air Act Amendments of 1977 and proposals for further legislation and regulation, particularly at the state level, have expanded interest in alcohols and ethers. Many new policy issues have arisen, and more are expected in the future. An important objective of this publication is to provide an updated and expanded technical assessment suitable as a foundation for policy discussion.

The transportation fuels industry has been shaped by four important events since 1976: a) the increased use of alcohols as blending components, b) the appearance of

marketplace concerns resulting from the misuse of alcohols as blending components, c) the appearance of federal environmental regulations over the composition of motor fuels, and d) the appearance of ethers as fuel components. In the future a fifth event may be added to these: the regulation of motor fuel composition based on health effects of fuel vapors and combustion products.

This technical assessment, therefore, has been expanded to include ethers as well as alcohols. It also considers flexible-fuel vehicles and vehicles intended for use with neat alcohols, neither of which had been developed in 1976.

This publication summarizes information from the technical literature on producing and applying alcohols and ethers as fuels and fuel components. The alcohols and ethers that are considered include a) methanol, ethanol, isopropyl alcohol (IPA), tertiary butyl alcohol (TBA), methyl tertiary butyl ether (MTBE) and tertiary amyl methyl ether (TAME) as fuel components; b) methanol (both neat and mixed with hydrocarbons) and ethanol as transportation fuels; and c) methanol in stationary power sources. This publication assesses the technical advantages and disadvantages of alcohols and ethers with respect to hydrocarbon fuels. The analysis also addresses the following factors: a) the costs associated with producing alcohols and ethers, b) distribution, storage, and fire protection and safety concerns, and c) health and environmental concerns.

CHAPTER 2—CHEMICAL AND PHYSICAL PROPERTIES OF ALCOHOLS AND ETHERS

General

The chemical and physical properties of alcohols and ethers useful as fuel or fuel components are described in this chapter. A sound understanding of the properties of alcohols and ethers and their effects in blends with hydrocarbons is critical to the use of such materials as motor fuels or fuel components.

The characteristic chemical difference between the components of hydrocarbon fuels and oxygenates, such as alcohols and ethers, is the presence of oxygen in the

molecule. The formulae and properties for some oxygenates are listed in Table 1. Additional properties are presented in Appendix B. Oxygenates differ substantially from hydrocarbons in such important fuel parameters as the amount of oxygen required to burn them and in the volumes of combustion products as shown in Table 2. In addition, alcohols and ethers, when burned, generate less heat per gallon than do hydrocarbons. The alcohols also require more heat for vaporization than do hydrocarbon fuels. Combustion performance also includes improved antiknock response, which is presently

Table 1—Some Properties of Oxygenates, Gasoline, and No. 2 Diesel Fuel

Property	Methanol	Ethanol	IPA	TBA	MTBE	TAMB	Gasoline	No. 2 Diesel Fuel
Formula	CH ₃ OH	C ₂ H ₅ OH	(CH ₃) ₂ CHOH	(CH ₃) ₃ COH	(CH ₃) ₃ COCH ₃	(CH ₃) ₂ (C ₂ H ₅)COCH ₃	C ₄ to C ₁₂	C ₈ to C ₂₅
Molecular weight	32.04	46.07	60.09	74.12	88.15	102.18	100-105	200 (approx.)
Composition, weight %								
Carbon	37.5	52.2	60.0	64.8	68.1	70.5	85-88	84-87
Hydrogen	12.6	13.1	13.4	13.6	13.7	13.8	12-15	13-16
Oxygen	49.9	34.7	26.6	21.6	18.2	15.7	0	0
Specific gravity, 60°F/60°F	0.796	0.794	0.789	0.791	0.744	0.77	0.72-0.78	0.81-0.89
Density, lb/gal @60°F	6.63	6.61	6.57	6.59	6.19	6.41	6.0-6.5	6.7-7.4
Boiling temperature, °F	149	172	180	181	131	187	80-437	370-650
Reid vapor pressure, psi	4.6	2.3	1.8	1.8	7.8	1.5	8-15	<0.2
Octane no. (see note b)								
Research octane no.	—	—	—	—	—	—	88-98	—
Motor octane no.	—	—	—	—	—	—	80-88	—
Cetane no. (see note b)	—	—	—	—	—	—	—	40-55
Water solubility, @70°F								
Fuel in water, volume %	100	100	100	100	4.3	—	Negligible	Negligible
Water in fuel, volume %	100	100	100	100	1.4	0.6	Negligible	Negligible
Viscosity								
Centipoise @60°F	0.59	1.19	2.38	4.2 @78°F	0.35	—	0.37-0.44	2.6-4.1
Centipoise @-4°F	1.15	2.84	9.41	Solid	0.60	—	0.60-0.77	9.7-17.6
Flash point, closed cup, °F	52	55	53	52	-14	—	-45	165
Autoignition temperature, °F	867	793	750	892	815	—	495	600 (approx.)
Flammability limits, volume %								
Lower	7.3	4.3	2.0	2.4	1.6	—	1.4	1.0
Higher	36.0	19.0	12.0	8.0	8.4	—	7.6	6.0
Latent heat of vaporization								
Btu/gal @60°F	3,340	2,378	2,100	1,700	863	—	900 (approx.)	710 (approx.)
Btu/lb @60°F	506	396	320	258	138	—	150 (approx.)	100 (approx.)
Heating value								
Lower (liquid fuel-water vapor) Btu/lb	8,570	11,500	13,300	14,280	15,100	15,690	18,000-19,000	18,000-19,000
Lower (liquid fuel-water vapor) Btu/gal @60°F	56,800	76,000	87,400	94,100	93,500	100,600	109,000-119,000	126,000-130,800
Stoichiometric air/fuel, weight	6.45	9.00	10.3	11.1	11.7	12.1	14.7	14.7
Ratio moles product/moles O ₂ + N ₂	1.21	1.12	1.10	1.10	1.10	1.09	1.08	1.07

Notes:

*See Appendix B for all references.

b Laboratory engine Research and Motor octane rating procedures are not suitable for use with neat oxygenates. Octane values obtained by these methods are not useful in determining knock-limited compression ratios for vehicles operating on neat oxygenates and do not represent octane performance of oxygenates when blended with gasolines. Similar problems exist for cetane rating procedures.

Table 2—Combustion of Alcohols, Ethers, and Hydrocarbons in Air

Fuel	Combustion Reaction Equation ^a
Methanol	$\text{CH}_3\text{OH} + 1.5\text{O}_2 + 5.64 \text{ N}_2 \longrightarrow$ $\text{CO}_2 + 2\text{H}_2\text{O} + 5.64 \text{ N}_2$
Ethanol	$\text{C}_2\text{H}_5\text{OH} + 3\text{O}_2 + 11.3 \text{ N}_2 \longrightarrow$ $2\text{CO}_2 + 3\text{H}_2\text{O} + 11.3 \text{ N}_2$
Isopropyl Alcohol	$\text{C}_3\text{H}_7\text{OH} + 4.5\text{O}_2 + 16.93 \text{ N}_2 \longrightarrow$ $3\text{CO}_2 + 4\text{H}_2\text{O} + 16.93 \text{ N}_2$
tert-Butyl Alcohol	$\text{C}_4\text{H}_9\text{OH} + 6\text{O}_2 + 22.6 \text{ N}_2 \longrightarrow$ $4\text{CO}_2 + 5\text{H}_2\text{O} + 22.6 \text{ N}_2$
MTBE	$\text{C}_5\text{H}_{12}\text{O} + 7.5\text{O}_2 + 28.2 \text{ N}_2 \longrightarrow$ $5\text{CO}_2 + 6\text{H}_2\text{O} + 28.2 \text{ N}_2$
TAME	$\text{C}_6\text{H}_{14}\text{O} + 9\text{O}_2 + 33.9 \text{ N}_2 \longrightarrow$ $6\text{CO}_2 + 7\text{H}_2\text{O} + 33.9 \text{ N}_2$
Gasoline or Diesel Fuel	$\text{C}_n\text{H}_{2n+2} + [(3n + 1)/2] \text{ O}_2 + 3.76 [(3n + 1)/2] \text{ N}_2 \longrightarrow$ $n\text{CO}_2 + (n + 1) \text{ H}_2\text{O} + 3.76 [(3n + 1)/2] \text{ N}_2$

Note:

^aBased on an air mixture of 79% nitrogen, 21% oxygen.

an objective of the use of oxygenates as substitutes for, or supplements to, gasoline.

As shown in Figure 1, all alcohols contain the same functional group as water—the OH, or hydroxyl, group. Consequently, like water, their molecules have polar characteristics. The molecular polarity is stronger for alcohols with a small hydrocarbon structure or a low carbon number. Methanol is the lowest-order alcohol in a homologous series. Ethanol is next. Alcohols with a large hydrocarbon structure (for example, TBA) have weak polarity. Neither gasoline nor MTBE contains the OH group; consequently, they have little or no significant polarity. While MTBE does contain oxygen, the oxygen is bound into the molecule differently than it is in alcohols. As shown in Figure 1, the oxygen in MTBE is bound into the carbon chain itself rather than being bound at the end of the chain as an OH group.

The physical phenomenon of molecular polarity has important consequences for blends of alcohols in hydrocarbons. Polar molecules have an affinity for other molecules in proportion to the degree of mutual polarity. Thus, at room temperatures, low molecular weight substances like water or methanol would be gases were they not collapsed into liquids by the highly cohesive

molecular forces of hydrogen bonding. However, when methanol is dissolved in a non-polar solvent like gasoline, its molecules become physically separated. This physical separation weakens molecular cohesion and the methanol behaves like a gas, resulting in an otherwise anomalous increase in vapor pressure that peaks at quite low methanol concentrations. If water is present as a second phase, a so-called "water bottom," the methanol's affinity for the highly polar water molecules will cause it to separate from the gasoline into the water phase. These effects are much less pronounced for ethanol and are insignificant for higher carbon number alcohols.

Heating Value

One of the most serious disadvantages to the substitution of oxygenates for motor gasoline, either as components or as a complete fuel, is their lower energy content and heating value. For example, the heating value of a gallon of methanol is about half that of a gallon of gasoline. Thus, at equivalent engine efficiency, a methanol-powered vehicle would be able to travel only about half the distance it could cover using the same volume of gasoline. For other oxygenates de-

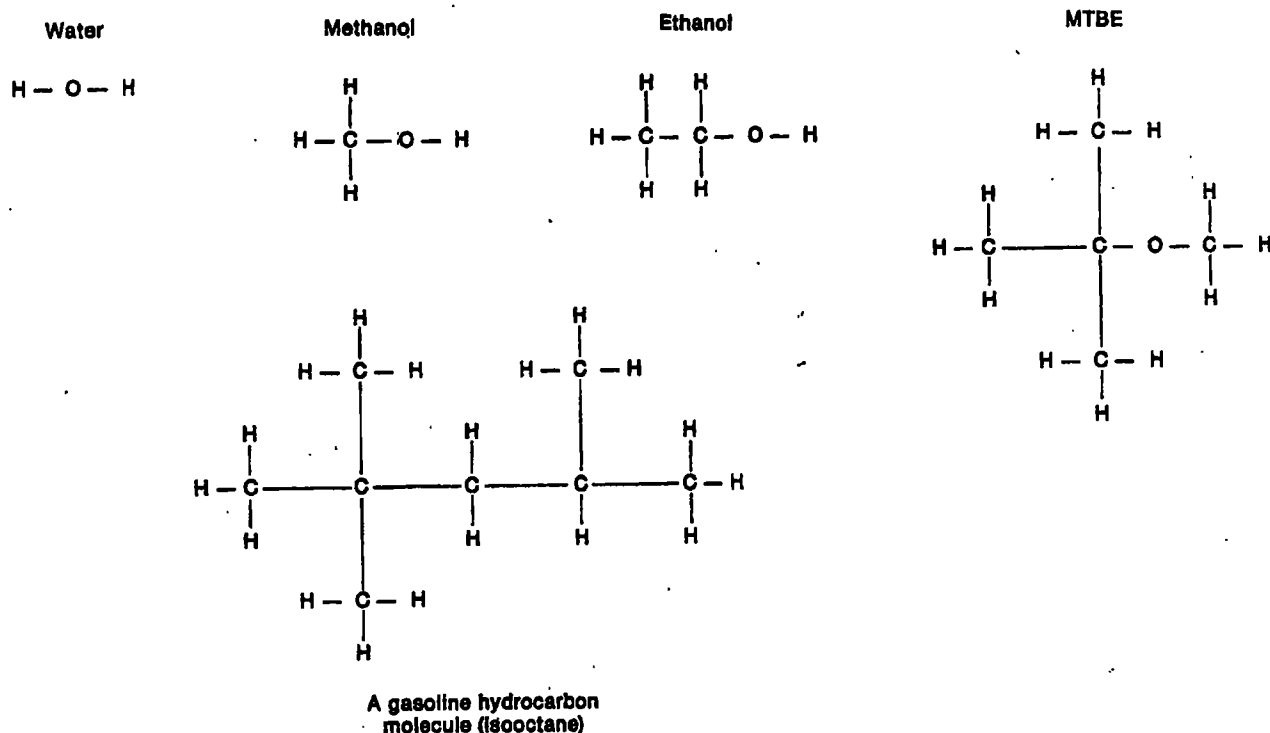


Figure 1—Molecular Structures of Water, Methanol, Ethanol, MTBE, and Gasoline

scribed in this publication, the mileage penalty is not as great and may not be considered serious when they are used as blending agents in concentrations approved by the Environmental Protection Agency (EPA).

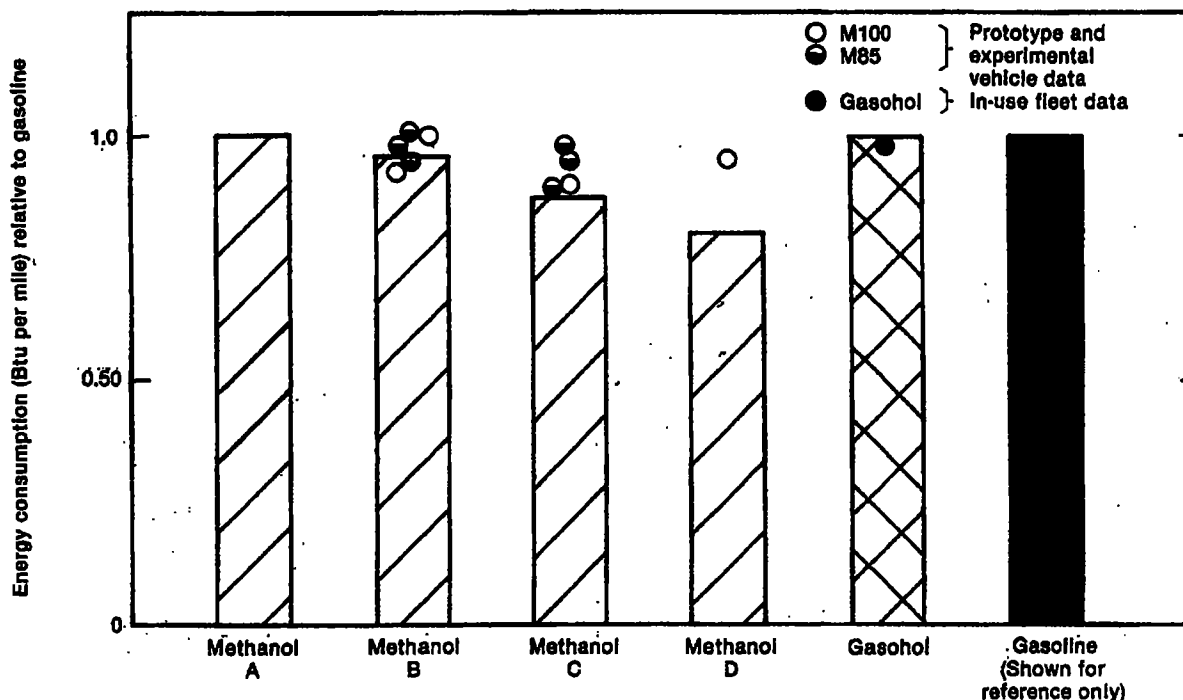
Figure 2 shows the fuel economy that has been obtained when neat methanol and M85, a mixture of 85 percent by volume methanol and 15 percent by volume gasoline, are used instead of gasoline. Because methanol allows improved engine efficiency, as discussed in Chapter 5, vehicle mileage usually is not reduced to the extent predicted by direct calculations based upon heating value differences alone. Furthermore, it has been demonstrated that engines and vehicles can be optimized to take advantage of the vaporization and combustion characteristics of neat methanol to recover additional tank mileage⁴⁻¹² (see Figure 2). If it is assumed that M85 allows the same improvements in engine efficiency that are theoretically expected through the use of neat methanol, a fully optimized vehicle would need about 1.5 times more gallons of M85 to travel the same distance as a comparable gasoline vehicle. However, as shown in Figure 2, even the most fuel efficient methanol vehicles presently require at least 1.7 times more M85 and 1.8 times more M100 to travel the same distance as a comparable gasoline vehicle.

Figure 3 shows the same information presented in Figure 2 in terms of energy consumption (Btu/mile). When viewed in this manner, the potential thermodynamic benefits of methanol as a motor fuel appear attractive. Ethanol also offers similar potential for increased engine efficiency; however, as covered in Chapter 3, it is not as economically attractive as methanol as a neat motor fuel.

Energy consumption comparisons from prototype and experimental vehicles are reviewed in Figure 3. Many of the vehicles demonstrated better utilization of potential fuel energy with methanol or M85 than with gasoline. Thermal efficiency improvements approaching 15 percent have been confirmed in some vehicles by means of increased compression ratio and improved combustion. Considerable engine and vehicle development will be required to confirm the theoretical thermal efficiency gains anticipated from lean mixture combustion with methanol.

Octane Performance

Oxygenates can be attractive for use as blending components to increase gasoline octane quality. Adding small percentages of oxygenates to gasoline can produce



Legend:

Methanol A—Relative energy consumption based on difference in energy content between gasoline and methanol.

Methanol B—Relative energy consumption assuming a 4 percent thermal efficiency improvement can be achieved due to improved combustion with methanol.

Methanol C—Relative energy consumption assuming a 15 percent thermal efficiency improvement can be achieved due to improved combustion and increased compression ratio with methanol.

Methanol D—Relative energy consumption assuming a 25 percent thermal efficiency improvement can be achieved due to improved combustion, increased compression ratio, and optimized lean mixture with methanol.

Source: References 3, 4, 5, 6, 7, 8, and 9.

Figure 3—Vehicle Energy Consumption (Btu per Mile) for Oxygenates Expressed Relative to That for Gasoline

Table 3—Octane Boost for Selected Oxygenates

Oxygenate	Concentration Limit (Volume Percent)	Basis for Limit	Typical Blending Value ^b (R + M)/2	Boost at Concentration Limit ^b
Ethanol	10.0	Gasohol Waiver (1979)	113	2.6
Methanol	0.3	Substantially Similar (1981)	116	0.1
Methanol/GTBA (1:1 ratio)	9.4 ^c	ARCO Waiver 3.5 weight percent oxygen (1981)	107	1.9
MTBE	11.0 ^c	Substantially Similar 2.0 weight percent oxygen (1981)	110	2.2

Notes:

^aSource: Reference 13.

^bOctane blending values vary with oxygenate concentration, base fuel octane, and composition. Octane boost is calculated for an 87 octane (R + M)/2 unleaded gasoline. See Glossary, Appendix A, Blending Value.

^cWill vary with base fuel density, since limited by weight percent oxygen.

The solubility of methanol in gasoline is affected by the chemical nature of the hydrocarbons that make up the gasoline. For example, methanol is fully soluble in n-hexane above 100°F, but only about 3 percent will dissolve in n-hexane at 40°F.^{15, 16} Methanol and n-octane are only sparingly soluble in each other over the same temperature range.

Methanol dissolves less readily in paraffinic hydrocarbons than it does in aromatic hydrocarbons as shown in Table 4.^{17, 18} The variability among gasolines in the ratios of paraffinic to aromatic hydrocarbons, therefore, is a complicating factor in the consideration of blends containing methanol above 5 percent by volume.

Ethanol and higher alcohols dissolve more readily in hydrocarbons than methanol does. They can be used as cosolvents to increase the solubility of methanol in gasoline.¹⁸⁻²⁴ For example, in a gasoline that dissolved only 3 percent by volume methanol at 32°F, 5 percent by volume isobutyl alcohol increased the methanol solubility to 20 percent by volume, and 5 percent by volume ethanol increased it to 10 percent by volume.

Volume Change of Mixtures of Alcohols and Gasoline

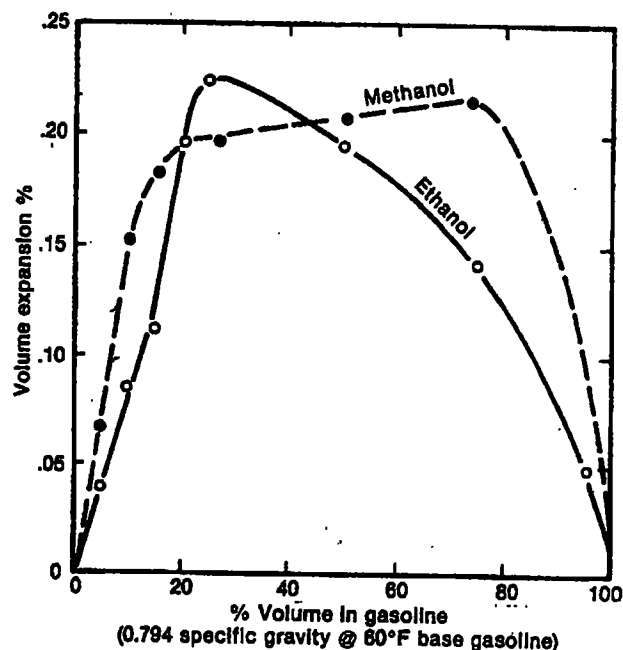
A small but measurable volume expansion effect occurs when alcohols, particularly methanol and ethanol, are added to hydrocarbons. The volume expansion is affected by the density of gasoline. As Figure 4 shows, the

Table 4—Solubility of Methanol in Gasoline

Aromatics in Gasoline, Volume Percent	Methanol Solubility, Volume Percent	
	-10° to 0°F	32° to 37°F
16	2-3	5-10
28	5-10	15-20
31	5-10	> 50
42	> 50	> 50

Gasoline Composition			Minimum Temperature At Which 10% Methanol Will Dissolve, °F
Saturates	Aromatics	Olefins	
100	—	—	80
65	21	14	44
43	2	55	20
20	78	2	4

Source: References 17 and 18.



Source: References 25 and 26.

Figure 4—Volume Increase for Gasoline-Alcohol Blends

expansion of a gasoline-methanol blend reaches a maximum value of about 0.2 percent over a broad range of concentrations from about 20 to 80 percent methanol. Gasoline-ethanol blends reach about the same maximum expansion but peak sharply at about 20 percent ethanol content.^{25, 26} Expansion values for gasoline-ethanol blends as high as 0.55 percent with a 12.5 percent concentration of ethanol have been observed.²⁷

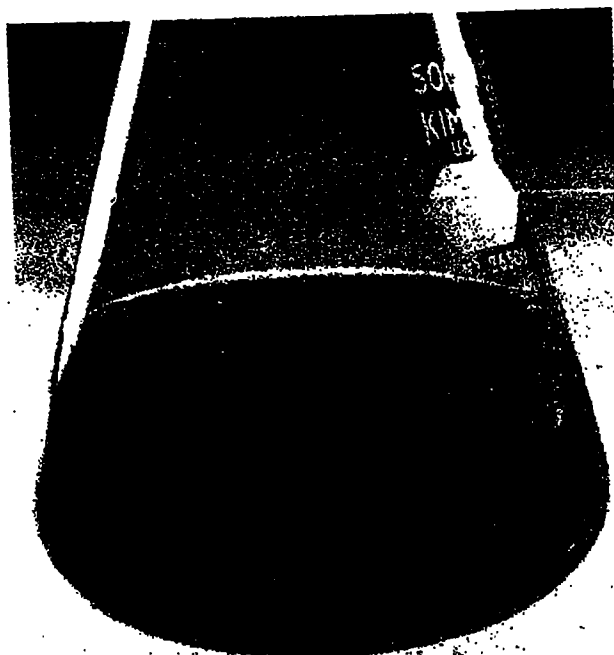
Water Sensitivity and Tolerance

The solubility of methanol in gasoline in the presence of water is very limited at room temperature. The solubility of ethanol is better than methanol but is also limited in the presence of water.^{25, 26, 28} When small amounts of water are added to a gasoline-methanol blend, hydrogen bonds form between water and methanol molecules and the blend separates into two phases. Paraffinic hydrocarbons predominate in the upper phase, while the lower phase consists primarily of alcohol, water, and small amounts of aromatic hydrocarbons. MTBE has little affinity for water and does not phase separate.

Data on the water sensitivity of gasoline-methanol blends show that blends containing 10 percent by volume methanol must be protected against water in

concentrations greater than 0.05 percent by volume at 70°F,²² or the blend will separate by the formation of droplets, as shown in Figure 5.²⁹ A number of higher molecular weight alcohols have been evaluated as cosolvent agents in attempts to increase water tolerance. The use of higher alcohols, including ethanol, as cosolvents to methanol markedly increases the amount of water that can be tolerated at a given temperature.³⁰ In addition the higher the combined concentration of alcohols, the greater the tolerance for water. Butyl alcohols are very effective cosolvents. Concentrations of 4.5 percent by volume of t-butyl alcohol in combination with 4.5 percent by volume of methanol increase water tolerance above 0.2 percent by volume. Figure 6 shows that water tolerance always increases with temperature.

As shown in Figure 7, the aromatics content of the base gasoline greatly influences the amount of water that can be tolerated without separation.²⁶ In the range of 14 to 38 percent aromatics content, with cosolvent present, each percent increase in aromatics content reduced the temperature for phase separation by 2–3°F. The benefit of aromatics content, as well as cosolvent



Blend phase separation

Source: Reference 29.

Figure 5—Gasoline-Alcohol Blend
Phase Separation

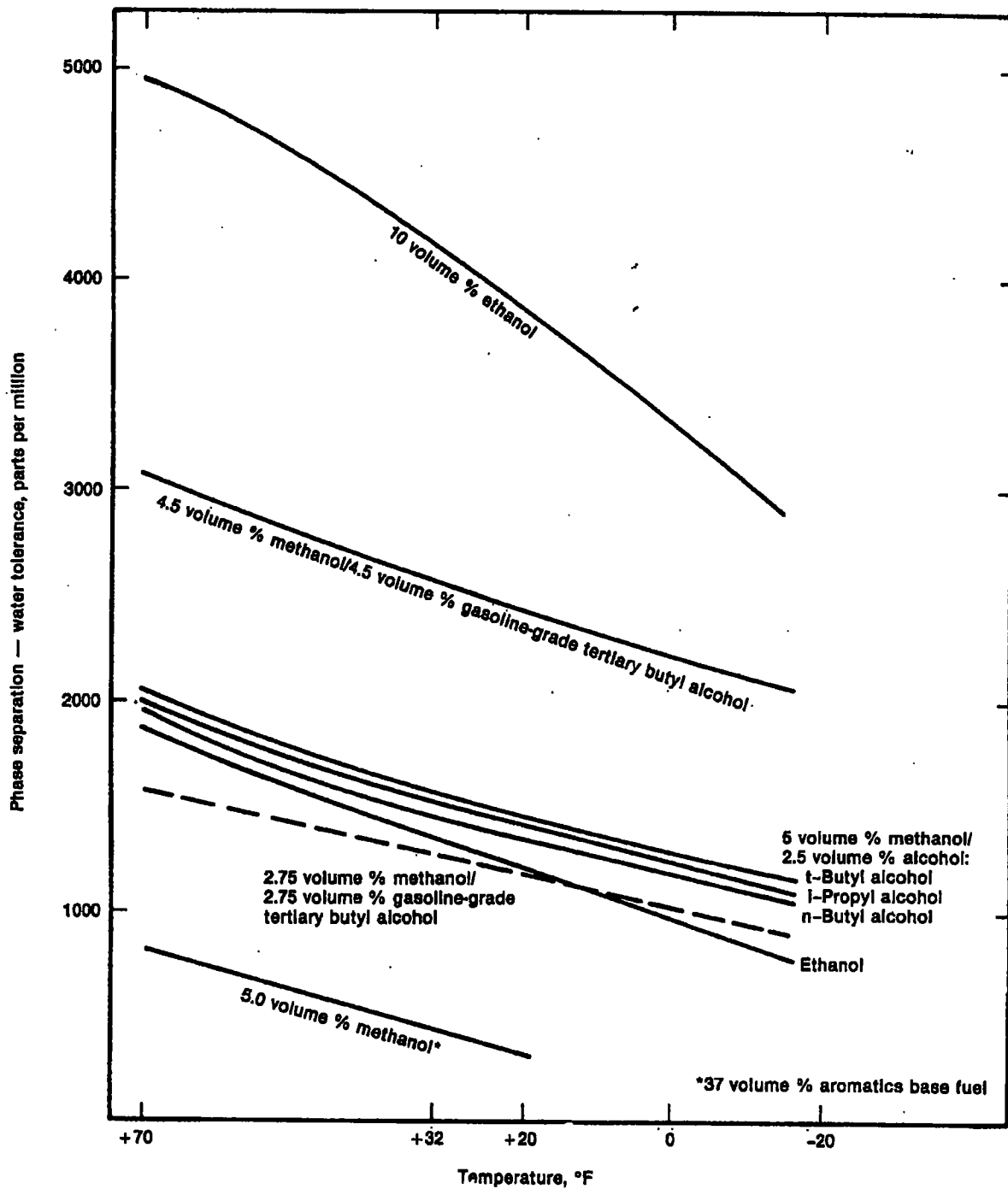
concentration, appears to be independent of temperature. An effective cosolvent increases water tolerance at all temperatures. Chapter 7 addresses water tolerance and separation in gasoline distribution systems.

Oxygenate Effects on Volatility

Methanol is a single compound that boils at 149°F. Ethanol is also a single compound and boils at 172°F. MTBE boils at 131°F. Gasoline, on the other hand, is a mixture of compounds that boils over a range of temperatures (generally 80–437°F). Thus, methanol and ethanol and the other oxygenates have constant volatilities, while the volatility of gasoline can be tailored over a range by adjusting the relative amounts of different hydrocarbons in the mixture. The difference in volatility between the oxygenates and gasoline is an important factor in the performance of gasoline-oxygenate blends in automobile engines with respect to starting, warmup, vapor lock, and other driveability characteristics. These effects are covered in detail in Chapter 4.

Adding alcohols to hydrocarbons or gasoline depresses the boiling temperature of individual hydrocarbons.³¹ The effect of alcohol addition on the shape of a distillation curve is shown in Figure 8.³² The light alcohols cause significant reduction in the temperatures for evaporation of the front end, which affects primarily the first 50 percent evaporated. Alcohols depress the boiling point of aromatic hydrocarbons slightly less than aliphatic hydrocarbons. Lower molecular weight alcohols have the greatest effect on boiling point depression. Methanol causes the largest changes; its effects can be observed even when accompanied by a cosolvent. Higher molecular weight alcohols such as TBA and ethers such as MTBE exert smaller changes on the distillation characteristics.

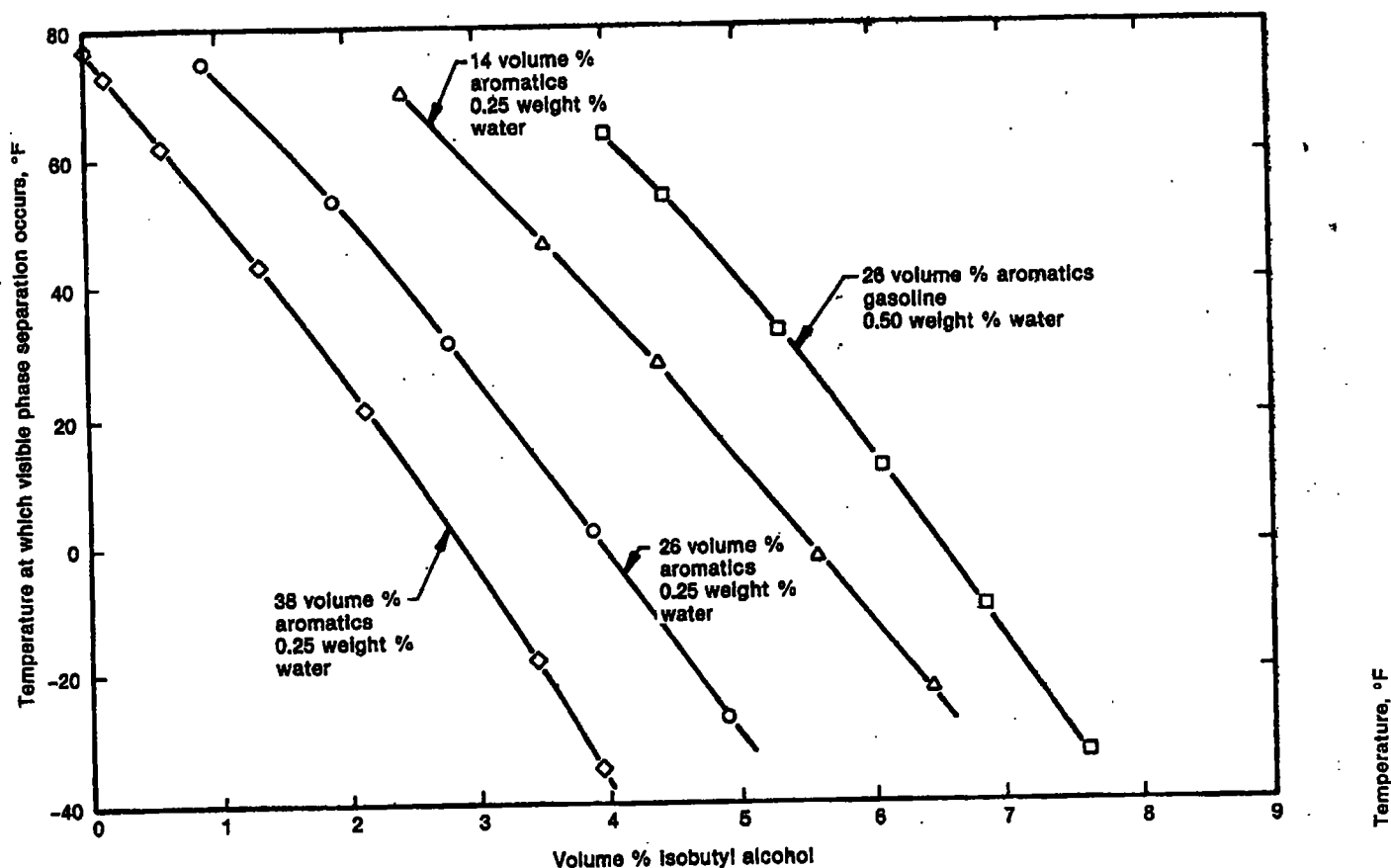
Vapor pressure is another important volatility parameter of gasoline that is adversely affected by the addition of alcohol. A common technique for measuring this parameter is the Reid Vapor Pressure (RVP) method, which involves determination of pressure in a closed chamber maintained at 100°F. As shown in Table 1, the RVP values listed for neat alcohols, ranging from 1.3–4.6 pounds per square inch (psi), appear low relative to that of motor gasoline with RVP values of 8–15 psi. However, blending alcohol into gasoline forms a nonideal solution that does not follow linear blending relationships. Rather than lowering vapor pressure, methanol and ethanol cause increases in RVP as illustrated in Figure 9.³² Methanol, at very low concentrations, typically generates an increase in RVP of 3 psi. Considering molecular polarity, the plateau-shaped



Notes:

1. Indolene base fuel — 30 percent aromatics.
2. Source: References 22 and 30.

Figure 6—Water Tolerance of Gasoline-Alcohol Blends



Source: Reference 26.

Figure 7—Effect of Cosolvent and Aromatics Content on Phase Separation of Blends With 10 Volume Percent Methanol

curve suggests that methanol vapors may exist in concentrations disproportionate to the alcohol concentration in the blend. Equal amounts of a cosolvent, such as TBA, blended with methanol mitigate the effect of methanol somewhat but still result in an RVP increase of over 2 psi. Ethanol produces RVP changes of about 1 psi in a 9 psi RVP gasoline, while TBA and MTBE have little effect on gasoline at this RVP level.

When methanol or ethanol is added, gasolines with lower vapor pressures incur larger increases in vapor pressure than gasolines with high vapor pressures. Figure 10 shows that the vapor pressure effect of methanol or ethanol on gasoline with 13 psi RVP is less than it is on a 9 psi RVP gasoline.^{31, 33} A partial explanation for this effect is that the alcohol mole fraction at the 10 volume percent level is lower in the 13 psi RVP blend than it is in the 9 psi RVP blend, since the 13 psi RVP

blend, with its higher concentration of lower molecular weight hydrocarbons, contains more moles per unit volume. The RVP increase is a function of alcohol mole fraction.

When gasoline-alcohol blends are commingled with gasoline, as they might be in routine product handling, the effects of the alcohol in the blend are similar to those discussed above.^{34, 35} Figure 11 shows that mixing gasoline-alcohol blends with gasoline of the same RVP results in substantially increased vapor pressure. This is due to the non-linear relationship between RVP increase and alcohol concentration over the concentration range of alcohol found in gasoline-alcohol blends and commingled product. The greatest increases in vapor pressure occurred in mixtures that contained about 20 percent of the gasoline-alcohol blend. The blend containing MTBE did not show increased vapor pressure.

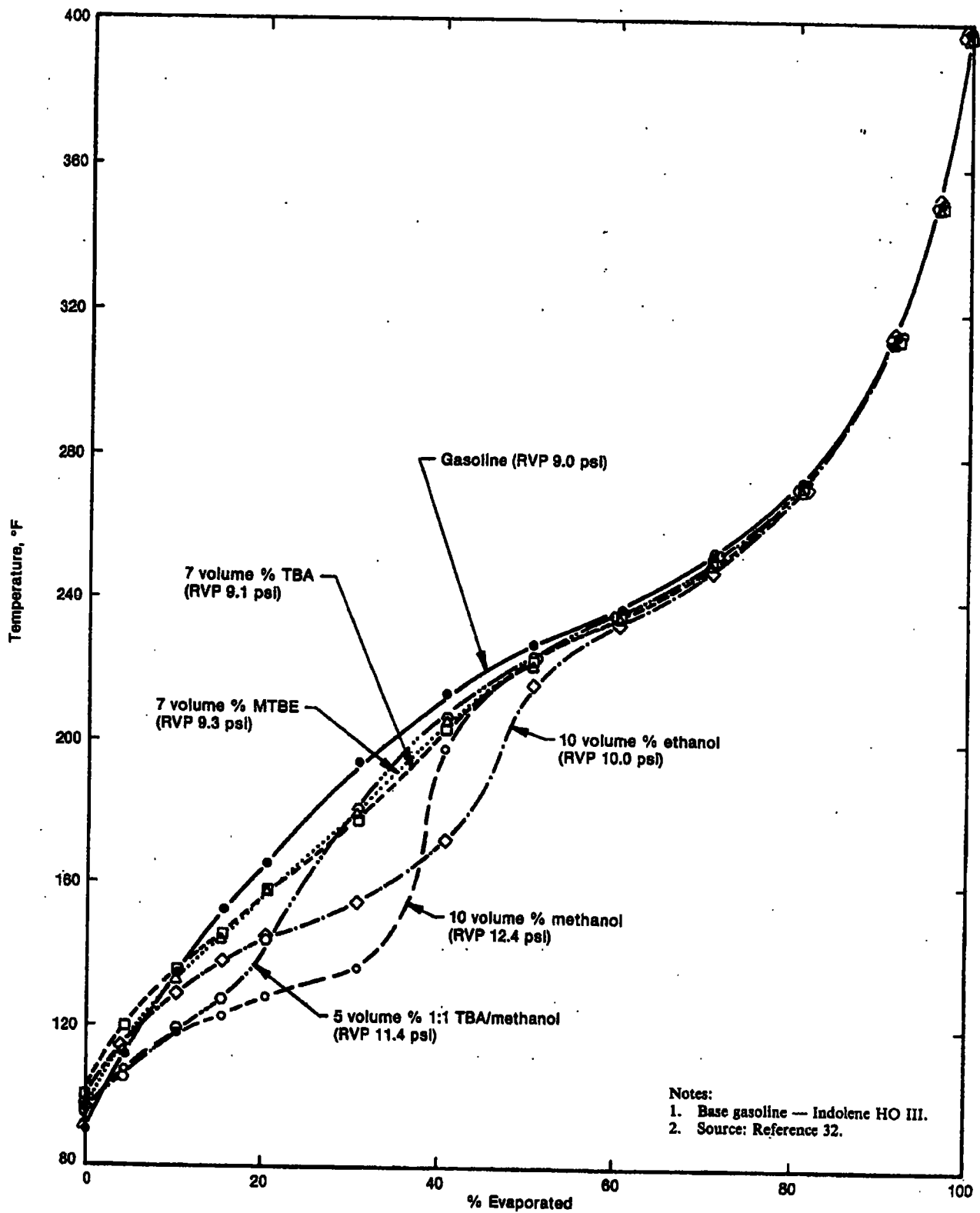
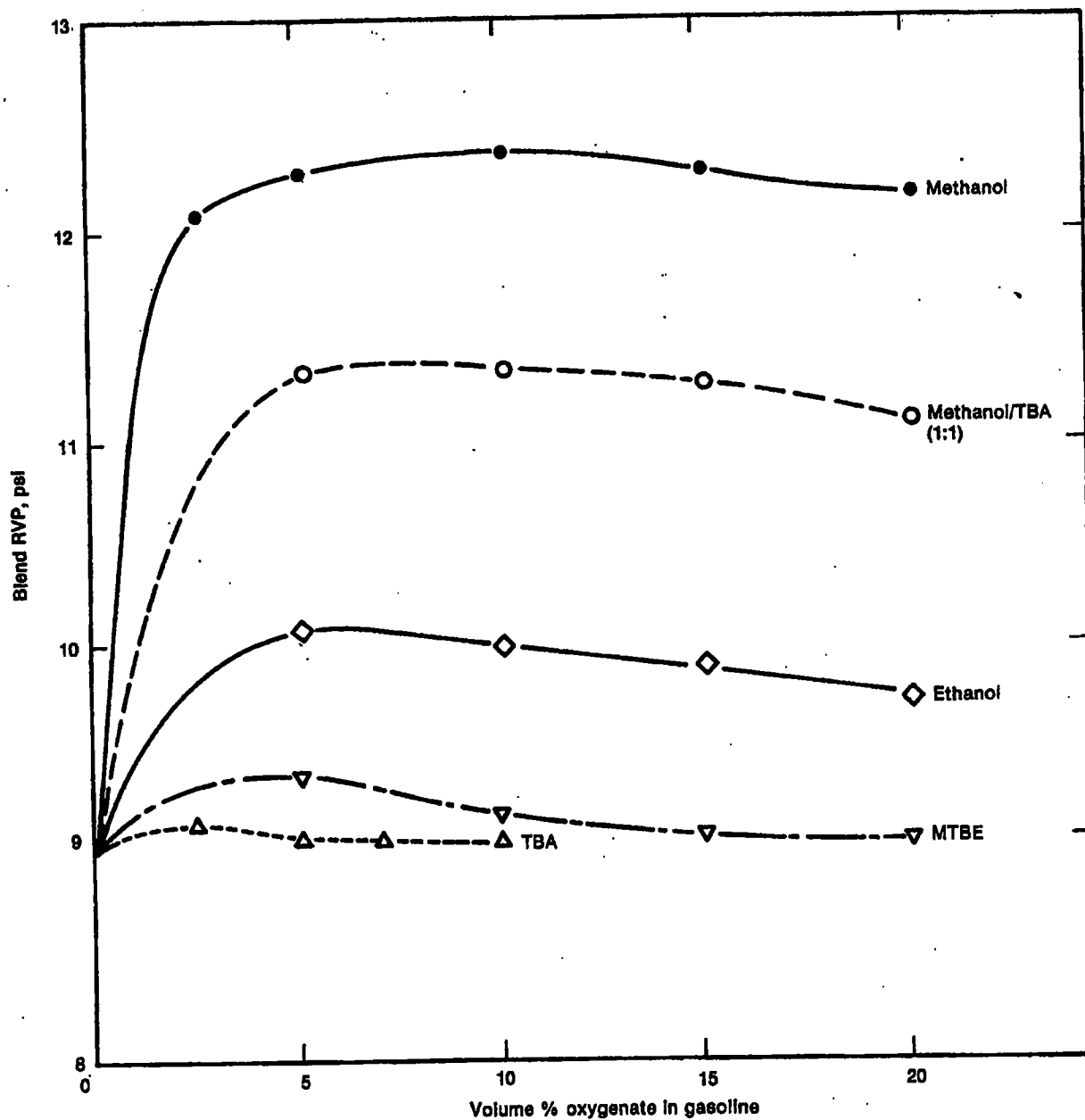


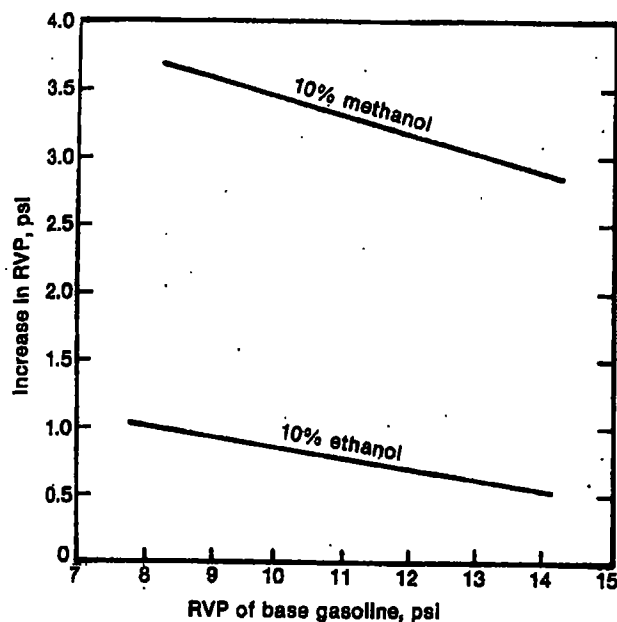
Figure 8—Effect of Oxygenates on Distillation



Notes:

1. Base gasoline — Indolene HO III.
2. Source: Reference 32.

Figure 9—Effect of Oxygenate Concentration on Blend Vapor Pressure



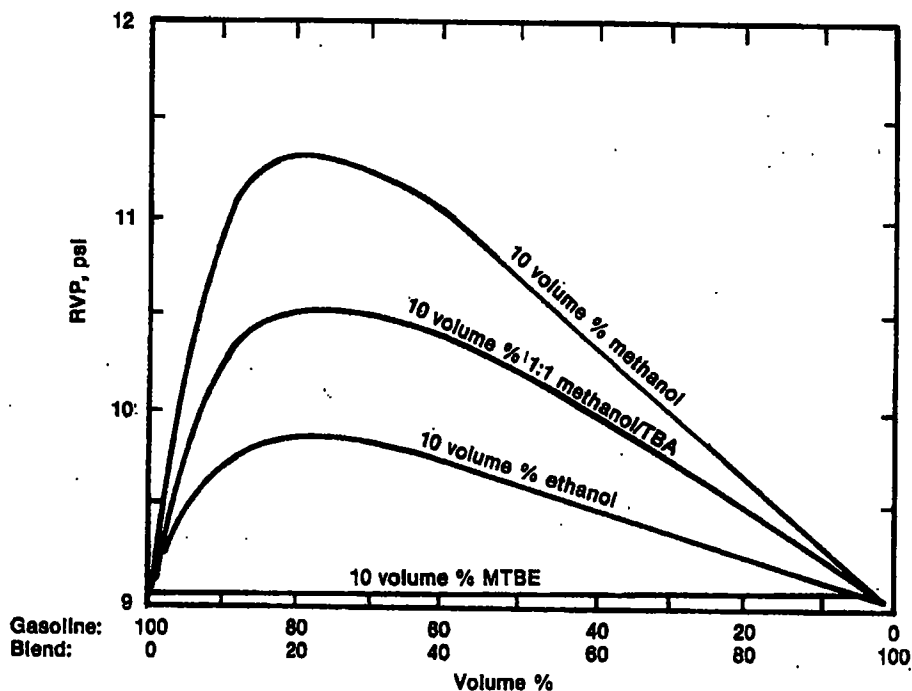
Source: References 31 and 33.

Figure 10—Effect of Base Gasoline RVP on RVP Boost Due to Alcohol Addition

Excessive vapor pressure may increase vehicle vapor lock and evaporative emissions as discussed in detail in Chapter 4. A gasoline volatility parameter, known as Vapor/Liquid (V/L) ratio, is a useful predictor of gasoline performance in a vehicle fuel system at high temperatures. The V/L ratio can be measured or it can be calculated for gasolines using a combination of distillation and vapor pressure characteristics.

Calculations of temperatures for specific V/L ratios of gasoline-alcohol blends using ASTM procedures developed for gasolines do not predict measured values. Figure 12 shows that the correlation of calculated versus measured temperatures for a V/L ratio of 20 ($T_{V/L=20}$) for gasoline and gasoline with MTBE is quite good.³⁶

Figure 13 shows how the addition of butane and alcohols changes the temperatures at which various V/L ratios occur. Higher temperatures for a given V/L ratio indicate better hot fuel handling properties. For example, the reference gasoline reaches a V/L ratio of 20 (the ratio that correlates best with vapor lock performance for most cars) at a temperature of 160°F. Adding 5 percent butane to the reference gasoline reduces the $T_{V/L=20}$ to 138°F, which is, coincidentally, the same



Source: Reference 35.

Figure 11—Effect of Commingling a Gasoline and a Gasoline-Oxygenate Blend of the Same RVP

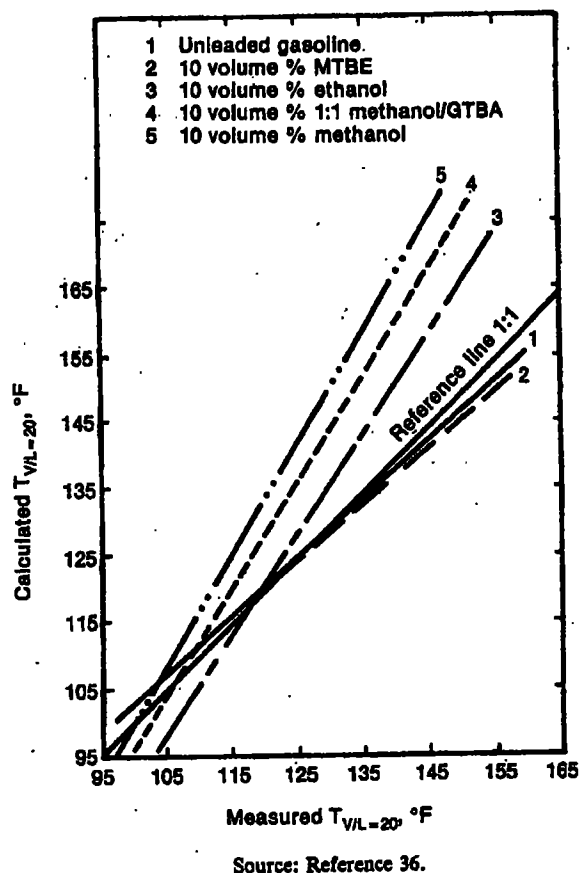


Figure 12—Calculated Versus Measured Temperature for a Vapor to Liquid Ratio of 20 ($T_{V/L-20}$)

temperature caused by the addition of 10 percent ethanol. Methanol causes a large decrease in the $T_{V/L-20}$ at concentrations as low as 2 percent. In practice a gasoline-methanol blend can be adjusted to achieve the same vapor-locking tendency as a base gasoline by removing all of the butanes and reducing the pentanes. However, doing so would negate the increase in gasoline volume or octane obtained by adding methanol and would still give a distillation curve with a prominent flat segment that could adversely affect vehicle driveability characteristics other than vapor lock—for example, cold-start driveability.

Gasoline-alcohol blends have unusual distillation curves and vapor pressures, and current performance assessment correlations developed with gasoline are not reliable. Chapters 4 and 5 will expand on the significance of the physical and thermal properties of alcohols and ethers on vehicle performance.

CHAPTER 3—OXYGENATES PRODUCTION TECHNOLOGY, CAPACITY, AND COSTS

Methanol

Worldwide methanol capacity in 1988 is about 440 thousand barrels per calendar day or 6.6 billion gallons per year. U.S. and Canadian capacities are about 110 and 42 thousand barrels per calendar day (1.6 billion and 650 million gallons per year), respectively. The major U.S. and Canadian producers of methanol are Borden, DuPont, Lyondell, Celanese, and Alberta Gas.³⁷ For perspective, U.S. consumption of gasoline and highway diesel fuel is 8400 thousand barrels per calendar day or 130 billion gallons per year.

Essentially all methanol worldwide is produced from natural gas. Technology also exists to manufacture methanol from coal, cellulosic refuse, or most types of

biomass.³⁸ In methanol production the feedstock is used to prepare a synthesis gas, either through reforming or catalytic partial oxidation. The synthesis gas is reacted over a catalyst at the proper pressure and temperature to produce methanol. The methanol is then dried and purified.

Natural gas requires little preparation for producing the synthesis gas. Other feedstocks, including coal, have to be sorted, screened, and pulverized before the synthesis gas step. Feedstocks other than natural gas also contain sulfur that has to be removed from the synthesis gas. Since natural gas often contains little sulfur, there may be no need for sulfur removal when natural gas is used as the feedstock. Figure 14 is a simplified diagram of the methanol production process.

EXHIBIT 2

United States Patent [19]

Jarvis et al.

US005679117A

[11] Patent Number: 5,679,117
[45] Date of Patent: Oct. 21, 1997

[54] REFINING PROCESS AND APPARATUS

[75] Inventors: David R. Jarvis, Coral Springs, Fla.;
Ewert J. A. Wilson, Albany, Ky.

[73] Assignee: Research Octane Inc., Albany, N.Y.

[21] Appl. No.: 734,091

[22] Filed: Oct. 21, 1996

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 605,282, Feb. 8, 1996, abandoned, which is a continuation-in-part of Ser. No. 430,275, Apr. 28, 1995, abandoned, which is a continuation-in-part of Ser. No. 385,466, Feb. 8, 1995, abandoned.

[51] Int. Cl.⁶ C10L 1/18

[52] U.S. Cl. 44/451; 585/1; 585/302

[58] Field of Search 44/451; 585/1; 585/302

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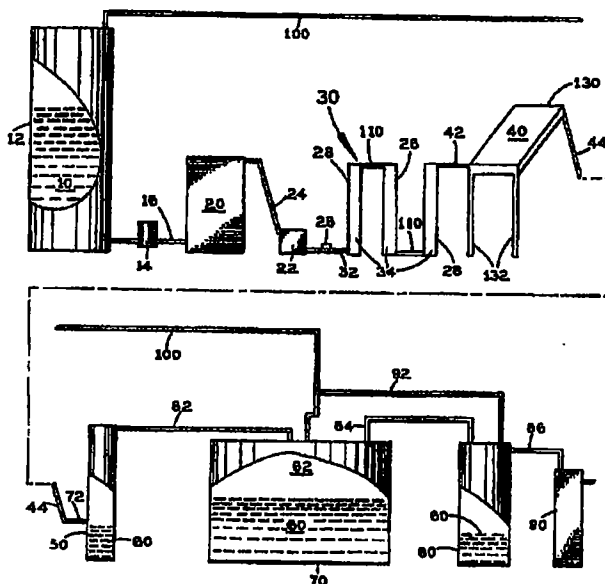
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5,310,954	5/1994	Hiles et al.	549/429
5,348,707	9/1994	Harandi et al.	44/449

Primary Examiner—Jacqueline V. Howard
Attorney, Agent, or Firm—Oltman, Flynn & Kubler

[57] ABSTRACT

A process of producing high octane hydrocarbons includes the steps of preparing a mixture of substantially ethanol and butane or natural gasoline, or low octane gasoline, the mixture having room temperature and atmospheric pressure, adjusting the pressure of the mixture to a magnitude within the range of 10 to 50 pounds per square inch, adjusting the temperature of the mixture to a magnitude within the range of 100 to 460 degrees Fahrenheit, adjusting the pressure of the mixture to a pressure within the range of 500 to 1000 hydrocarbons pounds per square inch, catalyzing the mixture with a platinum catalyst, lowering the temperature of the mixture to a magnitude within a range of 90 to 190 degrees Fahrenheit, and separating out liquid product and gas from the mixture. An apparatus for producing high octane alcohols includes a starting tank for retaining a mixture of substantially ethanol and butane or natural gasoline, or low octane gasoline, a heat exchanger for raising the temperature of the mixture, a first high pressure conduit extending from the starting tank to the heat exchanger, a catalyzing chamber, second and third high pressure conduits extending from the heat exchanger to the catalyzing chamber, a nozzle interconnecting the second and third high pressure conduits, high pressure pumps for extracting the heated mixture from the heat exchanger and delivering the mixture to the catalyzing chamber through the second and third high pressure conduits, and a separator for precipitating liquid product out of the mixture.

7 Claims, 1 Drawing Sheet



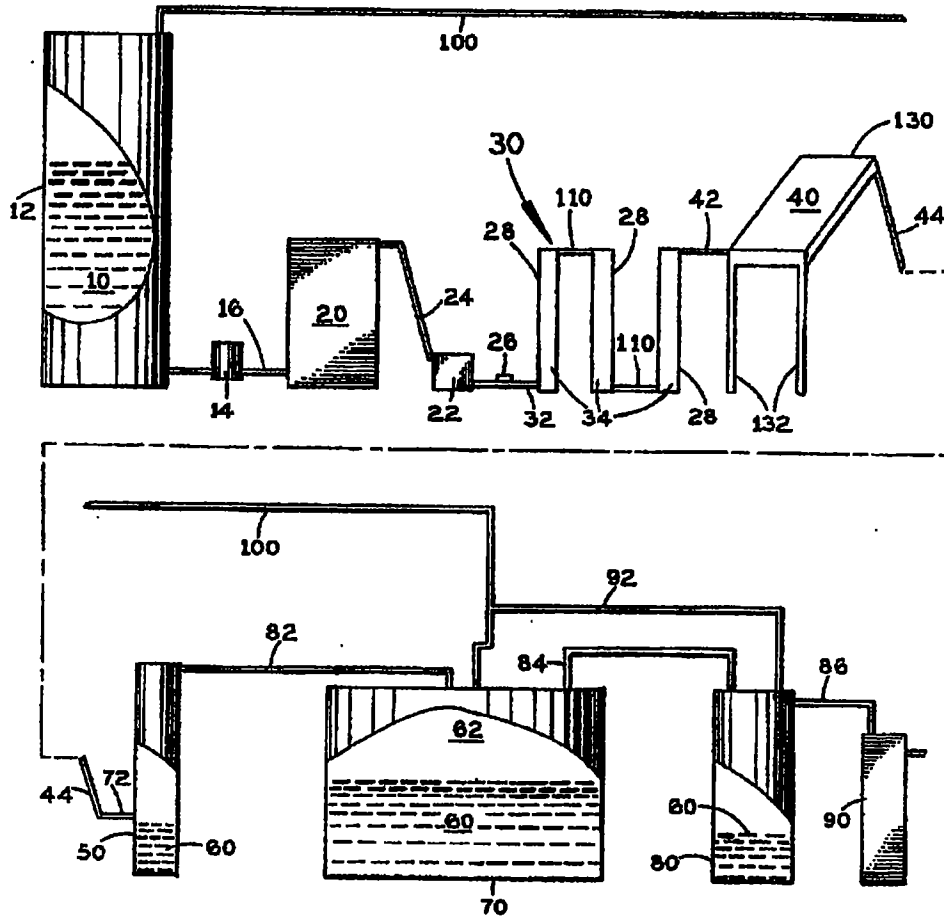


FIG. 1

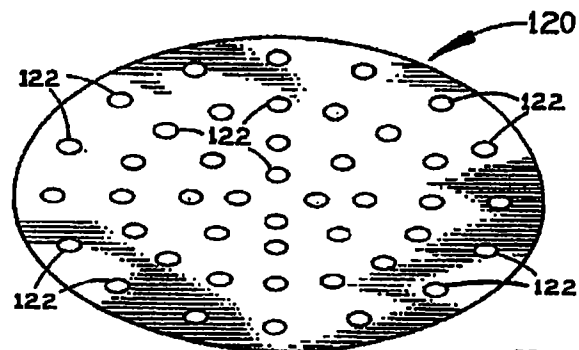


FIG. 2

REFINING PROCESS AND APPARATUS

The present invention is a continuation-in-part of Ser. No. 08/605,282, filed Feb. 8, 1996, now abandoned, which is a continuation-in-part of Ser. No. 08/430,275 filed Apr. 28, 1995, now abandoned, which is a continuation-in-part of Ser. No. 08/385,466, filed Feb. 8, 1995, now abandoned.

FIELD OF THE INVENTION

The present invention relates generally to the field of fuel forming processes. More specifically it relates to a process of producing high octane alcohols, or pump gasoline, including the steps of placing a pre-mixed mixture of ethanol and other alcohols, and butane or natural gasoline or straight run gasoline in a starting tank, raising the pressure of gases above the surface of the mixture to fifty pounds per square inch, pumping the mixture from the bottom of the starting tank through a first high pressure conduit into a heat exchanger where the temperature of the mixture is raised to a magnitude within the range of 100 to 460 degrees Fahrenheit, extracting the heated mixture from the heat exchanger with high pressure pumps which raise the mixture pressure to 500 to 1000 pounds per square inch, and feeding the heated and pressurized mixture through a second high pressure conduit through a nozzle and through a third high pressure conduit into an elongate catalyzing chamber containing a platinum catalyst. Additional steps include delivering the catalyzed mixture through a fourth high pressure conduit into a cooler for lowering the temperature to a magnitude within a range of 90 to 190 degrees Fahrenheit, feeding the cooled mixture through a fifth high pressure conduit into a series of separator tanks in which liquid final product collects in the tank bottoms and gas rises within the tanks above the surface of the liquid, and the liquid is drained off as the final product. The final product is 120 to 160 research octane, 110 to 129 motor octane, R & M about 148. In the case where low octane gasoline (straight run gasoline) is used as the starting material, the final product is a substantially higher octane gasoline called pump gasoline. In general, the starting material may be low octane hydrocarbon material, and the final product is higher octane hydrocarbon material.

BACKGROUND OF THE INVENTION

There have long been various chemical processes for producing gasoline and other fuels. A problem with these prior processes has been that they either fail to produce high octane gasoline, or they fail to do so efficiently.

These prior processes include that of Harandi, U.S. Pat. No. 5,171,912, issued on Dec. 15, 1992. Harandi discloses a process for the production of C+ gasoline from n-butane and propane. The Harandi process includes the steps of contacting a fresh feedstream including normal butane with shape selective medium pore zeolite catalyst particles under conditions sufficient to convert n-butane to an effluent stream including C+ alkanes; separating the effluent stream in a fractionator to recover an overhead stream including propane; contacting the propane stream and a fresh propane feedstream with shape selective, medium pore zeolite catalyst particles under conversion conditions sufficient to convert propane to a mixture including C+ alkanes; deethanizing the mixture and passing the deethanized product including C+ alkanes to the fractionator for separation concurrent with the effluent stream; recovering a bottom stream including C+ gasoline from the fractionator; preferably, distilling an intermediate stream including C

alkanes from the fractionator and recovering a stream including isobutane and a stream including unconverted normal butane; and recycling the unconverted normal butane to the normal butane feedstream to the integrated process.

Ward, et al., U.S. Pat. No. 4,393,259, issued on Jul. 12, 1983, reveals a process for converting propane or butane to gasoline. The Ward, et al. process includes the steps of passing feed hydrocarbon into a dehydrogenation zone; passing the entire dehydrogenation zone effluent including hydrogen and light by-products into a catalytic condensation zone where the resulting olefins are converted into dimers and trimers; passing the condensation zone effluent stream into a separation zone in which the dimers and trimers are concentrated into a product stream, with unconverted feed hydrocarbon and hydrogen being recycled to the dehydrogenation zone.

Vora, et al., U.S. Pat. No. 4,304,948, issued on Dec. 8, 1981, teaches a multi-step hydrocarbon conversion process for converting butane to gasoline. The process includes the steps of passing butane into a dehydrogenation zone and the entire dehydrogenation zone effluent is then passed into a catalytic condensation zone where butylene is converted into C and C hydrocarbons; commingling and separating the condensation zone effluent, a stripper overhead stream and an absorber bottoms stream into vapor and liquid portions; passing the liquid into the stripper and contacting the vapor portion with stripper bottoms liquid in an absorber; contacting the absorber overhead stream with liquid butane in a second absorber to remove C hydrocarbons and recycling the dehydrogenation zone; and debutanizing a portion of the stripper bottoms to yield the liquid butane and a gasoline product.

Capsuto, et al., U.S. Pat. No. 4,444,988, issued on Apr. 24, 1984, discloses the use of liquefied propane and butane or butane recycled to control the heat of reaction of converting olefins to gasoline and distillate. The Capsuto, et al. process uses beds and separates the effluent product from the beds into a gas in a liquid phase, cools the gas phase to form additional liquid and heat exchanges the liquid with the overhead gas from the separator.

Wilson, U.S. Pat. No. 5,093,533, issued on Mar. 3, 1992, reveals blended gasolines and a process for making the blended gasolines. The Wilson process involves mixing of a butane-pentane rich component, and natural gasoline component, and at least one octane-enhancing component. The mix is weathered during the blending operation to remove light-weight hydrocarbons including two, three and four-carbon components.

Hiles, et al., U.S. Pat. No. 5,310,954, issued on May 10, 1994, discloses a process for preparing tetrahydrofuran. The Hiles et al. process separates tetrahydrofuran from a feed mixture containing water, lower alkanol and tetrahydrofuran, which includes distilling the mixture in a first distillation zone at a first pressure; recovering from an upper part of the distillation zone a first vaporous mixture including water, lower alkanol and tetrahydrofuran; subjecting the material from the first vaporous mixture to condensation conditions in a condensation zone; passing condensate from the condensation zone to a second distillation zone operated at a second pressure higher than the first pressure; recovering from an upper part of the second distillation zone a second vaporous mixture including water, lower alkanol and tetrahydrofuran that has a lower concentration of tetrahydrofuran than the first vaporous mixture; and recovering from a lower part of the second distillation zone a stream including substantially pure tetrahydrofuran.

It is thus an object of the present invention to provide a process of producing a very high octane alcohol product efficiently.

It is another object of the present invention to provide such a process which can be practiced with conventional heat exchanger and separator tank equipment.

It is still another object of the present invention to provide such a process which is safe to practice.

It is finally an object of the present invention to provide such a process which is inexpensive to practice.

SUMMARY OF THE INVENTION

The present invention accomplishes the above-stated objectives, as well as others, as may be determined by a fair reading and interpretation of the entire specification.

A process of producing high octane hydrocarbon material is provided, including the steps of preparing a mixture of substantially ethanol and butane or natural gasoline, or straight run gasoline, the mixture having a room temperature and an atmospheric pressure, adjusting the pressure of the mixture to a magnitude within the range of 10 to 50 pounds per square inch, adjusting the temperature of the mixture to a magnitude within the range of 100 to 460 degrees Fahrenheit, adjusting the pressure of the mixture to a pressure within the range of 500 to 1000 pounds per square inch, catalyzing the mixture with a platinum catalyst, lowering the temperature of the mixture to a magnitude within a range of 90 to 190 degrees Fahrenheit, and separating out liquid product and gas from the mixture. The process preferably includes the additional steps of delivering a quantity of the gas separated from the liquid product into a furnace to supply heat required for the process, and the further additional steps of delivering a quantity of the gas separated from the liquid product into the mixture at the initial step of the process. The separating step preferably includes several separation steps of separating the mixture into liquid product and gas.

An apparatus for producing high octane alcohols is also provided, including a starting tank for retaining a mixture of substantially ethanol and butane or natural gasoline, a heat exchanger for raising the temperature of the mixture, a first high pressure conduit extending from the starting tank to the heat exchanger, a catalyzing chamber, second and third high pressure conduits extending from the heat exchanger to the catalyzing chamber, a nozzle interconnecting the second and third high pressure conduits, high pressure pumps for extracting the heated mixture from the heat exchanger and delivering the mixture to the catalyzing chamber through the second and third high pressure conduits, and a separator for precipitating liquid product out of the mixture.

The catalyzing chamber preferably includes several upright tubular segments, each tubular segment having a top portion and a bottom portion and containing the platinum catalyst, interconnection conduits interconnecting the tubular segments alternately across the top and bottom portions of the tubular segments, a baffle plate within at least one of the tubular segments, the baffle plate having several plate ports. The tubular segments each preferably include one baffle plate positioned within and across the top portion and the bottom portion of the tubular segment.

BRIEF DESCRIPTION OF THE DRAWINGS

Various other objects, advantages and features of the invention will become apparent to those skilled in the art from the following discussion taken in conjunction with the following drawings, in which:

FIG. 1 is a semi-schematic view of the preferred apparatus for carrying out each step of the inventive process.

FIG. 2 is a perspective view of the baffle plate for use in the catalyzing chamber tubular segments.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

As required, detailed embodiments of the present invention are disclosed herein; however, it is to be understood that the disclosed embodiments are merely exemplary of the invention which may be embodied in various forms. Therefore, specific structural and functional details disclosed herein are not to be interpreted as limiting, but merely as a basis for the claims and as a representative basis for teaching one skilled in the art to variously employ the present invention in virtually any appropriately detailed structure.

Reference is now made to the drawings, wherein like characteristics and features of the present invention shown in the various FIGURES are designated by the same reference numerals.

Process

Referring to FIG. 1, a process of producing high octane alcohols is disclosed, including the following steps. A premixed mixture 10 of one third ethanol and two thirds butane at room temperature and atmospheric pressure is placed in a starting tank 12. The pressure of gases above the surface of the mixture 10 is raised to fifty pounds per square inch. The mixture 10 is pumped with pumps 14 from the bottom of starting tank 12 through a first high pressure conduit 16 into a heat exchanger 20, where the temperature of mixture 10 is raised to a level within the range of 100 to 460 degrees Fahrenheit. The preferred temperature is 225 degrees Fahrenheit. The heated mixture 10 is extracted from heat exchanger 20 with high pressure pumps 22, which raise mixture 10 pressure to a level within the range of 500 to 1000 pounds per square inch. The preferred pressure is 600 pounds per square inch. The heated and pressurized mixture 10 is fed through a second high pressure conduit 24, through a nozzle 26 and through a third high pressure conduit 32 into an elongate catalyzing chamber 30 containing a platinum catalyst 34. Chamber 30 includes three interconnected upright segments 28. The catalyzed mixture 10 is delivered through a fourth high pressure conduit 42 into a cooler 40 for lowering the mixture 10 temperature to a level within a range of 90 to 190 degrees Fahrenheit.

The cooled mixture 10 is fed through a fifth high pressure conduit 44 into a first separator tank 50 in which final liquid product 60 collects in the bottom of first separator tank 50 and gas 62 rises to fill a space within tank 50 above the surface of liquid product 60. The liquid product 60 is fed through a first separated liquid conduit 72 at the bottom of tank 50 and the gas 62 is drained off through a first separated gas conduit 82 at the top of tank 50. Both liquid product 60 and gas 62 are delivered into a second separator tank 70, in which more liquid product 60 is separated. Some of gas 62 within second separator tank 70 is delivered back through a feedback conduit 100 into the top of starting tank 12. Some of gas 62 within the second separator tank 70 is simultaneously delivered through a second separated gas conduit 84 into a third separator tank 80 where still more liquid product 60 precipitates out and gathers in the bottom of third separator tank 80. Some of gas 62 within third separator tank 80 is drained into a feedback conduit branch 92. Some of gas 62 within third separator tank 80 is delivered through a third

separated gas conduit 86 into a furnace 90, where gas 62 is burned as fuel to supply heat to the process where needed.

Final liquid product 60 is within the range of 120 to 160 research octane, 110 to 129 motor octane, and about 148 R and M. Other final product 60 test data are as follows:

Oxygenates	L.V. %	42.75
MTBE	L.V. %	<0.1
TAME	L.V. %	<0.1
Alcohols (Ethanol)	L.V. %	42.75
<hr/>		
G.C. Breakdown	Wt %	Vol %
N. Butane	45.60	53.03
ISO Pentane	1.42	1.55
N. Pentane	1.02	1.10
Toluene	2.02	1.57
Ethanol	49.94	42.75
<hr/>		
PONA	Vol %	
Paraffins	55.68	
Olefins	0.01	
Naphthenes	<0.01	
Aromatics	1.57	

To produce high octane gasoline, add 20% by volume of the new product to 80 octane gasoline. The resulting mixture is 92.8 octane, with a vapor pressure in the range of 4 to 19 pounds per square inch.

Preferred Embodiments of Apparatus

Referring to FIG. 1, a preferred apparatus is disclosed for practicing the above-described process of producing high octane alcohols. This apparatus is merely exemplary and other forms of apparatus are contemplated.

Starting tank 12 is a vertical cylindrical drum. Heat exchanger 20 and pumps 14 and 22 are of any suitable conventional design. Nozzle 26 is preferably about three eights inches diameter. Catalyzing chamber 30 includes three elongate, upright tubular segments 28, each containing platinum catalyst 34. Segments 28 are interconnected by interconnection conduits 110, across the tops of the first and second segments 28 and across the bottoms of second and third segments 28. A baffle plate 120 having a plurality of ports 122 is positioned across the top and bottom of each segment 28. See FIG. 2. Cooler 40 preferably includes a substantially horizontal tray 130 elevated on legs 132. Separator tanks 50, 70 and 80 are vertical cylindrical drums. Tank 70 is preferably of substantially larger diameter than tanks 50 and 80.

Another embodiment of the invention uses as a starting material approximately one third ethanol mixed with two thirds natural gasoline. The process and apparatus for treating this mixture is the same as that previously described and this explanation will not be repeated herein. Natural gasoline is essentially a mixture of butanes and pentanes plus other hydrocarbon materials. Natural gasoline is derived from wet gas by stripping it. An example of natural gasoline is as follows:

C6+ . . . 53.871% by liquid volume
Butane . . . 3.03% by liquid volume
Neo-pentane . . . 0.697% by liquid volume
Iso-pentane . . . 26.046% by liquid volume
Normal pentane . . . 16.349% by liquid volume.

The resulting product is substantially one half natural gasoline and one half ethanol. It has a vapor pressure of 1.5 to 8.0 psi and an octane rating of 108 to 160.

A further embodiment uses as a starting material a mixture of 10% ethanol and 90% natural gasoline. The process steps and apparatus remain the same. The resulting product showed an increase in octane rating from 72 to 80-100.

It has been found that the starting material may contain 5% to 50% ethanol, and 50% to 95% natural gasoline. It is possible to add to the mixture 3% to 40% butane. The resulting product contains 5-50% ethanol, 50-90% natural gasoline including 3% to 50% hydrocarbons, and a trace of aromatics. The resulting product has a higher octane rating than the starting material. The product has an acceptable vapor pressure. This product appears to be a gasoline grade product. The ethanol can be removed without harming the product.

In the first embodiment, pentane, including iso-pentane, may be substituted for butane in the starting material. In another embodiment, the starting material is a low octane hydrocarbon material known as light gasoline or straight run gasoline having an octane rating in the vicinity of 65 to 70. This material is processed through the apparatus described above and in the same way as described in connection with the first and further embodiments. One additional option is to inject a small amount of hydrogen in the catalyst bed. It has been found that the process increases the octane rating of the hydrocarbon material to a level in the vicinity of 87, such that the final product is pump gasoline. The final product has a vapor pressure in the range from 6 to 8 psi which is an acceptable range.

While the invention has been described, disclosed, illustrated and shown in various terms or certain embodiments or modifications which it has assumed in practice, the scope of the invention is not intended to be, nor should it be deemed to be, limited thereby and such other modifications or embodiments as may be suggested by the teachings herein are particularly reserved especially as they fall within the breadth and scope of the claims here appended.

We claim:

1. A process of producing high octane alcohols, comprising the steps of:

preparing a mixture of low octane hydrocarbon material, having an octane rating in the vicinity of 65 to 70, said mixture having room temperature and atmospheric pressure,

adjusting said pressure of said mixture to a magnitude within the range of 10 to 50 pounds per square inch, adjusting said temperature of said mixture to a magnitude within the range of 100 to 460 degrees Fahrenheit,

adjusting the pressure of said mixture to a pressure within the range of 500 to 1000 pounds per square inch,

catalyzing said mixture with a platinum catalyst, lowering the temperature of said mixture to a magnitude within a range of 90 to 190 degrees Fahrenheit,

separating out liquid product and gas from said mixture.

2. A process according to claim 1, comprising the additional step of:

delivering a quantity of said gas separated from said liquid product into furnace means to supply heat required for said process.

3. A process according to claim 1, comprising the additional steps of:

delivering a quantity of said gas separated from said liquid product into said mixture at the initial step of said process.

4. A process according to claim 1, wherein said separating step comprises a plurality of separation steps of separating said mixture into liquid product and gas.

5,679,117

7

5. A method according to claim 1, wherein said hydrocarbons comprise butane.

6. A method according to claim 1, wherein said hydrocarbons comprise natural gasoline.

8

7. A method according to claim 1, wherein said hydrocarbons comprise straight run gasoline.

* * * * *

EXHIBIT 3

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Applicant:

**CHARLES A. LIEDER
LLOYD E. FUNK
DAVID A. BARKER**

§
§ **Group Art Unit: 1714**
§

§ **Examiner: Cephia D. Toomer**
§

Filed: April 21, 2000

Serial No.: 09/556,852

**For: GASOLINE-OXYGENATE BLEND
AND METHOD OF PRODUCING
THE SAME**

§
§
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§
§
§
§
§
§ **Attorney Docket No.: 013129/00025**

DECLARATION OF CHARLES A. LIEDER, Ph.D., UNDER 37 C.F.R. 1.132

I Charles A. Lieder do hereby state:

1. I am over the age of 18;
2. I received a Ph.D. degree in Physical Chemistry from Stanford University in 1974. I further received a B.A. degree in Chemistry and Math from Hope College in 1970.
3. I have been employed by Shell Oil Company ("Shell") since 1974. My first position at Shell was as a Research Scientist in Reaction/Environmental Engineering. Since that time, I have served as a Supervisor for Process Development, Technical Manager in Process Engineering, an Operations Manager in Crude/Diesel/Hydrogen/Sulfur, a Senior Staff Engineer to Fuels Regulatory Technical Support and an Engineering Advisor in Gasoline/Fuels Blending Technology. From 1989 to 1990, I was an "Executive-on-Loan" to the California Energy Commission.
4. I am a co-inventor of the above-referenced patent application and am familiar with the claims as presently pending before the U.S. Patent and Trademark Office. I am also familiar with the claims as amended and the new claims added to this application, as set forth in the contemporaneously filed Amendment and Response to Office Action of 10 September 2004. All of the presently pending claims are directed to a blend of a gasoline and an oxygenate wherein the Dry Vapor Pressure Equivalent is less than about 7.2 PSI.

5. I have read and reviewed U.S. Patent No. 5,679,117 ("*Jarvis*"). *Jarvis* discloses a "final liquid product 60" prepared by subjecting a mixture of ethanol and butane or natural gasoline to processing conditions in the presence of a platinum catalyst. (Line 25 of column 4 through line 24 of column 5.)

6. The Table in column 5 of *Jarvis* indicates that the amount of n-butane in the "final liquid product 60" is 53.03 volume percent and the amount of ethanol is 42.75 volume percent. The "final liquid product 60" of the Table is a blend of 53.03 volume percent of n-butane and 42.75 volume percent of ethanol. The minimum RVP of "final liquid product 60" is approximately 37.16:

Component	Known RVP of Component	Approx. Mole Fraction	RVP x Approx. Mole Fraction
n-butane	54	0.53	28.62
Ethanol	18	0.43	7.74
Pentanes	20	0.04	0.80

Total: 37.16 = RVP of Mixture

7. *Jarvis* discloses in lines 25-28 of column 5 that a high-octane gasoline may be prepared by adding 20% by volume of final liquid product 60 to 80 octane gasoline to render a resulting mixture having 92.8 octane "with a vapor pressure in the range of 4 to 19 pounds per square inch." The theoretical RVP of 20% by volume of "the new product" would, at best, be 7.4 (0.20×37.16). A high-octane gasoline having a vapor pressure between 4 to 7.4, based on this disclosure in *Jarvis*, is scientifically impossible.

8. In lines 65-67 of column 5 of *Jarvis*, the patentees provide an example wherein the resulting product is "substantially one half natural gasoline and one half ethanol". The RVP of such a product would be outside of the claimed ranges of the present application. The blending RVP of ethanol is 18.0. The natural gasoline, as described in lines 49-64, contains 53.871% by liquid volume C6+, 3.03% by liquid volume butane, 0.697% liquid volume neo-pentane, 26.046% by liquid volume iso-pentane and 16.349% by liquid volume normal pentane. The (approximate) calculated RVP of the natural gasoline is as follows:

Component	Known RVP of Component	Approx. Mole Fraction	RVP x Approx. Mole Fraction
C6+	11	0.539	5.93
Butane	54	0.03	1.62
Neo-pentane	31	0.007	0.22
Iso-pentane	19	0.26	4.94
n-pentane	16	0.163	2.61

Total: 15.32psi = RVP of Mixture

The theoretical RVP for the product containing one half of such natural gasoline and one half of ethanol would therefore be 16.66 PSI:

Component	Known RVP of Component	Approx. Mole Fraction	RVP x Approx. Mole Fraction
Gasoline	15.3	0.50	7.66
Ethanol	18	0.50	9.0

Total: 16.66psi = RVP of Mixture

The statement in lines 65-67 of *Jarvis* that the resulting product has a vapor pressure between 1.5 and 8.0 psi is incorrect. A blend of 50% ethanol and 50% of the stated gasoline formulation could not render a product having a vapor pressure less than 16.66 PSI.

9. Lines 27-28 of column 6 of *Jarvis* describes a "pump gasoline" wherein the "final product has a vapor pressure in the range from 6 to 8 psi which is an acceptable range." "Pump gasoline" is defined in *Jarvis* as a high-octane gasoline (line 11 of column 1). Specifications for high-octane gasoline for use as pump gasoline in service stations available to the U.S. public, for the time period February 8, 1995 to October 21, 1996¹, are set forth in ASTM D 4814-95c, "Standard Specification for Automotive Spark-Ignition Engine Fuel", copy attached as *Exhibit A*. It is unclear as to whether "final product" in line 26 of *Jarvis* refers to "final liquid product 60" or a high-octane. I would infer, however, that "final product" refers to a high-octane gasoline since *Jarvis* concludes that the "final product is pump gasoline" (line 26 of column 6). However, an admixture of "final liquid product 60" and a hydrocarbon stream could not render a "pump gasoline" having a vapor pressure in the range from 6 to 8 psi in accordance with the standards set forth in ASTM D 4814-95c.

¹ *Jarvis* matured from U.S. Patent Application Serial No. 734,091, filed on October 21, 1996; the parent application to U.S. Patent Application Serial No. 734,091 was filed on February 8, 1995.

As set forth in paragraph 6 above, "Final liquid product 60" has a calculated RVP of 37.16 psi. In order to comply with the maximum ethanol concentration of 10 volume percent as set forth by the EPA in Table 11 on page 24 of API Publication, Second Edition, July 1988, attached to the Amendment filed on August 24, 2001, only about 20 volume percent of "Final liquid product 60" could be used in admixture with a second hydrocarbon stream. As set forth in paragraph 7 above, 20% by volume of "Final liquid product 60" would have a RVP of 7.4 psi and 10 volume percent ethanol (49.94×0.20). In order for the RVP of the "final product" to be less than 8 psi (the "final liquid product 60" having a RVP of 7.4 psi), the remaining 80 volume percent of the other hydrocarbon stream would have to have a RVP < 0.6 psi. The hydrocarbon stream to meet this objective would likely be jet fuel or jet fuel constituents, such as a C₉-C₁₁ hydrocarbon stream containing nonane, decane and/or hendane.

Even in such instances, while the RVP would be < 8 psi; the mid-distillation point (T-50) of the "final product" would violate the standards set forth in D 4814 95c. The T-50 set forth in D 4814 95c must be less than 250° F, and the T-50 of the "final product" would be greater than 300° F. The resulting "final product" could therefore not be considered a "pump gasoline".

Further, the "final product" would be considered a "gap" fuel because it contains two different components (high volatility and low volatility) and thus lacks molecules in the mid-range distillation region. Gap fuels have poor startup and enhanced stalling characteristics. These characteristics defined the driveability of gasoline. The "final product" of lines 20-28 of column 6 of *Jarvis* would not pass the driveability recommendations of D 4814 95c or the internal specifications of common carrier pipelines in the U.S.

It can therefore be concluded that even if the "final product", referenced in lines 27-28 of column 6 of *Jarvis*, had a Dry Vapor Pressure Equivalent less than 7.2 PSI, the admixture could not be classified as a "pump gasoline".

The conclusions expressed in this paragraph would be the same using the current specifications for "Pump Gasoline" for use in the United States, as set forth in ASTM D 4814-04a, "Standard Specification for Automotive Spark-Ignition Engine Fuel", copy attached as *Exhibit B*.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and believe are believe to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are

punishable by fine or imprisonment, or both, under 18 U.S.C. 1001 and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

DATED: December 13, 2004

Charles A. Lieder
Charles A. Lieder, Ph.D.

EXHIBIT A



Designation: D 4814 – 04a

An American National Standard

Standard Specification for Automotive Spark-Ignition Engine Fuel¹

This standard is issued under the fixed designation D 4814; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

This standard has been approved for use by agencies of the Department of Defense.

1. Scope*

1.1 This specification covers the establishment of requirements of automotive fuels for ground vehicles equipped with spark-ignition engines.

1.2 This specification describes various characteristics of automotive fuels for use over a wide range of operating conditions. It provides for a variation of the volatility and water tolerance of automotive fuel in accordance with seasonal climatic changes at the locality where the fuel is used. For the period May 1 through September 15, the maximum vapor pressure limits issued by the U.S. Environmental Protection Agency (EPA) are specified for each geographical area except Alaska and Hawaii. Variation of the antiknock index with seasonal climatic changes and altitude is discussed in Appendix X1. This specification neither necessarily includes all types of fuels that are satisfactory for automotive vehicles, nor necessarily excludes fuels that can perform unsatisfactorily under certain operating conditions or in certain equipment. The significance of each of the properties of this specification is shown in Appendix X1.

1.3 The spark-ignition engine fuels covered in this specification are gasoline and its blends with oxygenates, such as alcohols and ethers. This specification does not apply to fuels that contain an oxygenate as the primary component, such as Fuel Methanol (M85). The concentrations and types of oxygenates are not specifically limited in this specification. However, depending on oxygenate type, as oxygenate content increases above some threshold level, the likelihood for vehicle problems also increases. The composition of both unleaded and leaded fuel is limited by economic, legal, and technical consideration, but their properties, including volatility, are defined by this specification. In addition, the composition of unleaded fuel is subject to the rules, regulations, and Clean Air Act waivers of the U.S. Environmental Protection Agency (EPA). With regard to fuel properties, including volatility, this specification can be more or less restrictive than the EPA rules,

regulations, and waivers. Refer to Appendix X3 for discussions of EPA rules relating to fuel volatility, lead and phosphorous contents, deposit control additive certification, and use of oxygenates in blends with unleaded gasoline. Contact the EPA for the latest versions of the rules and additional requirements.

1.4 This specification does not address the emission characteristics of reformulated spark-ignition engine fuel. Reformulated spark-ignition engine fuel is required in some areas to lower emissions from automotive vehicles, and its characteristics are described in the research report on reformulated spark-ignition engine fuel.² However, in addition to the legal requirements found in this research report, reformulated spark-ignition engine fuel should meet the performance requirements found in this specification.

1.5 This specification represents a description of automotive fuel as of the date of publication. The specification is under continuous review, which can result in revisions based on changes in fuel, automotive requirements, or test methods, or a combination thereof. All users of this specification, therefore, should refer to the latest edition.

NOTE 1—If there is any doubt as to the latest edition of Specification D 4814, contact ASTM International Headquarters.

1.6 Tests applicable to gasoline are not necessarily applicable to its blends with oxygenates. Consequently, the type of fuel under consideration must first be identified in order to select applicable tests. Test Method D 4815 provides a procedure for determining oxygenate concentration in mass percent. Test Method D 4815 also includes procedures for calculating mass oxygen content and oxygenate concentration in volume percent. Appendix X4 provides a procedure for calculating the mass oxygen content of a fuel using measured oxygenate type, oxygenate concentration in volume percent, and measured density or relative density of the fuel.

1.7 The following applies to all specified limits in this standard: For purposes of determining conformance with these specifications, an observed value or a calculated value shall be rounded "to the nearest unit" in the right-most significant digit used in expressing the specification limit, in accordance with

¹ This specification is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.A0 on Gasoline and Oxygenated Fuels.

Current edition approved July 1, 2004. Published August 2004. Originally approved in 1988. Last previous edition approved in 2003 as D 4814-04.

² Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1347.

*A Summary of Changes section appears at the end of this standard.

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TABLE 1 Vapor Pressure and Distillation Class Requirements

Vapor Pressure/ Distillation Class	Vapor Pressure, ^A max, kPa (psi)	Distillation Temperatures, °C (°F), at % Evaporated, max ^B					Distillation Residue, volume % , max	Driveability Index, ^C max, °C (°F) Derived ^{D,E}
		10 volume %, max	50 volume %		90 volume %, max	End Point, max		
			min	max				
AA	54(7.8)	70.(158.)	77.(170.)	121.(250.)	190.(374.)	225.(437.)	2.	597. (1250.)
A	62(9.0)	70.(158.)	77.(170.)	121.(250.)	190.(374.)	225.(437.)	2.	597. (1250.)
B	69(10.0)	85.(148.)	77.(170.)	118.(245.)	180.(374.)	225.(437.)	2.	591. (1240.)
C	79(11.5)	80.(140.)	77.(170.)	116.(240.)	185.(365.)	225.(437.)	2.	586. (1230.)
D	93(13.5)	65.(131.)	88.(160.)	113.(235.)	185.(365.)	225.(437.)	2.	580. (1220.)
E	103(15.0)	50.(122.)	66.(150.)	110.(230.)	185.(365.)	225.(437.)	2.	569. (1200.)

^A Consult EPA for approved test methods for compliance with EPA vapor pressure regulations.

^B At 101.3 kPa pressure (760 mm Hg).

^C Driveability Index (DI) = $1.5 T_{10} + 3.0 T_{50} + 1.0 T_{90}$, where T_{10} = distillation temperature, °C (°F), at 10 % evaporated, T_{50} = distillation temperature, °C (°F), at 50 % evaporated, and T_{90} = distillation temperature, °C (°F), at 90 % evaporated.

^D The DI specification limits are applicable at the refinery or import facility as defined by 40 CFR Part 80.2 and are not subject to correction for precision of the test method.

^E Since DI is an index and has no units, the standard temperature conversion from U.S. customary to SI units is not appropriate. The following equation is to be used to make the conversion: $DI_C = (DI_F - 176)/1.8$

the rounding method of Practice E 29. The use of a trailing decimal point in a limit indicates that the digit preceding the decimal point is a significant digit.

1.8 The values stated in SI units are the standard, except when other units are specified by federal regulation. Values given in parentheses are provided for information only.

NOTE 2—Many of the values shown in Table 1 were originally developed using U.S. customary units and were subsequently soft-converted to SI values. As a result, conversion of the SI values will sometimes differ slightly from the U.S. customary values shown because of round-off. In some cases, federal regulations specify non-SI units.

2. Referenced Documents

2.1 ASTM Standards:³

- D 86 Test Method for Distillation of Petroleum Products at Atmospheric Pressure
- D 130 Test Method for Corrosiveness to Copper from Petroleum Products by the Copper Strip Test
- D 287 Test Method for API Gravity of Crude Petroleum and Petroleum Products (Hydrometer Method)
- D 381 Test Method for Gum Content in Fuels by Jet Evaporation
- D 439 Specification for Automotive Gasoline⁴
- D 525 Test Method for Oxidation Stability of Gasoline (Induction Period Method)
- D 1266 Test Method for Sulfur in Petroleum Products (Lamp Method)
- D 1298 Test Method for Density, Relative Density (Specific Gravity), or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method
- D 2533 Test Method for Vapor-Liquid Ratio of Spark-Ignition Engine Fuels
- D 2622 Test Method for Sulfur in Petroleum Products by Wavelength Dispersive X-ray Fluorescence Spectrometry
- D 2699 Test Method for Research Octane Number of Spark-Ignition Engine Fuel

³ For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

⁴ Withdrawn.

D 2700 Test Method for Motor Octane Number of Spark-Ignition Engine Fuel

D 2885 Test Method for Determination of Octane Number of Spark-Ignition Engine Fuels by On-Line Direct Comparison Technique

D 3120 Test Method for Trace Quantities of Sulfur in Light Liquid Petroleum Hydrocarbons by Oxidative Microcoulometry

D 3231 Test Method for Phosphorus in Gasoline

D 3237 Test Method for Lead in Gasoline by Atomic Absorption Spectrometry

D 3341 Test Method for Lead in Gasoline-Iodine Monochloride Method

D 4052 Test Method for Density and Relative Density of Liquids by Digital Density Meter

D 4815 Test Method for Determination of MTBE, ETBE, TAME, DIPE, tertiary-Amyl Alcohol and C₁ to C₄ Alcohols in Gasoline by Gas Chromatography

D 4953 Test Method for Vapor Pressure of Gasoline and Gasoline-Oxygenate Blends (Dry Method)

D 5059 Test Methods for Lead in Gasoline by X-Ray Spectroscopy

D 5188 Test Method for Vapor-Liquid Ratio Temperature Determination of Fuels (Evacuated Chamber Method)

D 5190 Test Method for Vapor Pressure of Petroleum Products (Automatic Method)

D 5191 Test Method for Vapor Pressure of Petroleum Products (Mini Method)

D 5453 Test Method for Determination of Total Sulfur in Light Hydrocarbons, Motor Fuels, and Oils by Ultraviolet Fluorescence

D 5482 Test Method for Vapor Pressure of Petroleum Products (Mini Method-Atmospheric)

D 5500 Test Method for Vehicle Evaluation of Unleaded Automotive Spark-Ignition Engine Fuel for Intake Valve Deposit Formation

D 5598 Test Method for Evaluating Unleaded Automotive Spark-Ignition Engine Fuel for Electronic Port Fuel Injector Fouling

D 5599 Test Method for Determination of Oxygenates in Gasoline by Gas Chromatography and Oxygen Selective

D 4814 – 04a

TABLE 2 Detailed Requirements for All Volatility Classes^a

Lead Content, max, g/L (g/U.S. gal) ^a		Copper Strip Corrosion, max No. 1	Solvent-washed Gum Content, mg/100 mL, max 5	Sulfur, max, mass %		Oxidation Stability, Minimum, minutes 240.	Water Tolerance °
Unleaded	Leaded			Unleaded	Leaded		
0.013(0.05)	1.1(4.2)	No. 1	5	0.0350 ^c	0.15	240.	°

^a See Appendix X1 for information on Antiknock Index.

^b See Appendix X3 for U.S. EPA maximum limits for lead and phosphorus contents in unleaded gasoline (X3.2.1) and maximum average lead limits for leaded gasoline (X3.2.2).

^c Qualified small refineries have varying maximum sulfur limits up to 0.0450 mass % which are based on their 1997-1998 sulfur level baseline. If values are found in excess of 0.0350 mass %, it is the supplier's responsibility to provide proof that the source was a qualified small refinery.

^d Water tolerance limits in terms of maximum temperature for phase separation are given in Table 13.

Flame Ionization Detection

D 5845 Test Method for Determination of MTBE, ETBE, TAME, DIPE, Methanol, Ethanol, and *tert*-Butanol in Gasoline by Infrared Spectroscopy

D 6422 Test Method for Water Tolerance (Phase Separation) of Gasoline-Alcohol Blends

D 6469 Guide for Microbial Contamination in Fuels and Fuel Systems

E 29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications

2.2 Government Standard:

CFR 40 Code of Federal Regulations⁵

2.3 Other Standard:

CCR Title 17, §60100-§60114 California Code of Regulations⁶

3. Terminology

3.1 Definitions:

3.1.1 *antiknock index*, *n*—the arithmetic average of the Research octane number (RON) and Motor octane number (MON), that is, (RON + MON)/2.

3.1.2 *gasoline*, *n*—a volatile mixture of liquid hydrocarbons, generally containing small amounts of additives, suitable for use as a fuel in spark-ignition, internal combustion engines.

3.1.3 *gasoline-alcohol blend*, *n*—a fuel consisting primarily of gasoline along with a substantial amount (more than 0.35 mass % oxygen, or more than 0.15 mass % oxygen if methanol is the only oxygenate) of one or more alcohols.

3.1.4 *gasoline-ether blend*, *n*—a fuel consisting primarily of gasoline along with a substantial amount (more than 0.35 mass % oxygen) of one or more ethers.

3.1.5 *gasoline-oxygenate blend*, *n*—a fuel consisting primarily of gasoline along with a substantial amount (more than 0.35 mass % oxygen, or more than 0.15 mass % oxygen if methanol is the only oxygenate) of one or more oxygenates.

3.1.6 *oxygenate*, *n*—an oxygen-containing, ashless, organic compound, such as an alcohol or ether, which can be used as a fuel or fuel supplement.

3.1.7 *refinery*, *n*—a plant at which gasoline or diesel fuel is produced.

3.1.7.1 *Discussion*—This definition is from CFR 40 Part 80.2. In the federal definition, a plant not only covers the conventional refinery, but also covers oxygenate blending and other facilities where gasoline is produced.

⁵ Available from U.S. Government Printing Office, Superintendent of Documents, 732 N. Capitol St., NW, Mail Stop: SDE, Washington, DC 20401.

⁶ Available from Barclays, 50 California Street, San Francisco, CA 94111.

3.2 *Applicability*—To determine when a fuel contains a substantial amount of an oxygenate, a gasoline-oxygenate blend is defined as a fuel that contains more than 0.35 mass % oxygen, or more than 0.15 mass % oxygen if methanol is the only oxygenate. The definitions in this section do not apply to fuels that contain an oxygenate as the primary component; for example, fuel methanol (M85).

NOTE 3—The criteria in 3.2 were selected with consideration given to current oxygenate levels in the marketplace, state labeling practices, and consistency with federal legislation and regulations.

NOTE 4—Refer to Test Method D 4815 to calculate the mass oxygen content of a fuel using oxygenate concentration in mass %. Refer to Appendix X4 to calculate mass oxygen content of a fuel using oxygenate concentration in volume %.

4. Ordering Information

4.1 The purchasing agency shall:

4.1.1 State the antiknock index as agreed upon with the seller,

4.1.2 Indicate the season and locality in which the fuel is to be used,

4.1.3 Indicate the lead level required (Table 2), and

4.1.4 State the concentration and types of oxygenates present as agreed upon with the seller.

5. Performance Requirements

5.1 Some requirements and test methods applicable to automotive spark-ignition engine fuel depend on whether the fuel is a gasoline, or a gasoline-oxygenate blend. Test Methods D 4815 and D 5599, gas chromatographic test methods, are the recommended procedures to detect the types and amounts of oxygenates. Once the type of fuel is known, the appropriate requirements and test methods can be identified by reference to Table 1, Table 3, and Section 7.

5.2 Volatility of fuels is varied for seasonal climatic changes and conformance to U.S. EPA volatility regulations by providing six vapor pressure/distillation classes and six vapor lock protection classes for fuel. Volatility of fuel is specified by an alphanumeric designation that uses a letter from Table 1 and a number from Table 3.

5.2.1 The seasonal and geographic distribution of the combined vapor pressure/distillation-vapor lock classes is shown in Table 4. Tables 5-7 show the federal ozone nonattainment areas at several vapor lock protection levels that require reduced vapor pressure in the summertime. Tables 8-11 show at several vapor lock protection levels the areas that require federal reformulated spark-ignition engine fuel in the summertime.

TABLE 3 Vapor Lock Protection Class Requirements

Vapor Lock Protection Class	Vapor/Liquid Ratio (V/L) ^{a,b}	
	Test Temperature, °C (°F)	V/L, max
1	60.(140.)	20
2	58.(133.)	20
3	51.(124.)	20
4	47.(116.)	20
5	41.(105.)	20
6	35.(95.)	20

^a At 101.3 kPa pressure (760 mm Hg).

^b The mercury confining fluid procedure of Test Method D 2533 shall be used for gasoline-oxygenate blends. Either glycerin or mercury confining fluid may be used for gasoline. Test Method D 5188 may be used for all fuels. The procedure for estimating temperature-V/L (see Appendix X2) may only be used for gasoline.

Table 12 shows the areas with restrictive local vapor pressure limits that have been approved under the EPA state implementation plan (SIP).

5.2.2 The EPA vapor pressure regulations can cause the distillation of the fuel to be less volatile, which for some vehicles, results in a worse warm-up driveability performance.

5.2.3 Driveability Index (DI) is intended to provide control of distillation parameters that influence cold start and warm-up driveability. It is a function of the 10 %, 50 %, and 90 % evaporated distillation temperatures measured by Test Method D 86.

5.2.4 Test Method D 2533 contains procedures for measuring temperature-V/L of both gasoline and gasoline-oxygenate blends. For gasoline-oxygenate blends, the procedure requires that mercury be used as the confining fluid in place of glycerin. Either confining fluid may be used for gasoline. Test Method D 5188 is an alternative method for determining vapor-liquid ratio temperatures by an evacuated chamber method for gasoline-oxygenate blends, as well as gasoline. In case of dispute, Test Method D 2533 is the referee method. The method for estimating temperature-V/L (see Appendix X2) is only applicable for gasoline.

5.3 Antiknock index (AKI) is very important to engine performance. The matching of engine octane requirement to fuel octane level (AKI) is critical to the durability and performance of engines; this cannot be accomplished with a single specified minimum level of antiknock index. Appendix X1 includes a discussion of antiknock indexes of fuels currently marketed and relates these levels to the octane needs of broad groups of engines and vehicles. Also discussed is the effect of altitude and weather on vehicle antiknock requirements.

5.4 Additional fuel requirements are shown in Table 2.

5.5 The properties of gasoline-oxygenate blends can differ considerably from those of gasoline. Consequently, additional requirements are needed for gasoline-oxygenate blends. These requirements involve evaluation of compatibility with plastic and elastomeric materials in fuel systems, corrosion of metals, and especially in the case of gasoline-alcohol blends, water tolerance. Requirements for metal corrosion (other than copper) and material compatibility are not given because test methods and appropriate limits are still under development. When these have been developed, they will be included in this specification. Water tolerance is specified in Table 13.

5.6 Depending on oxygenate type and concentration in the blend, vehicle driveability with gasoline-oxygenate blends can differ significantly from that with gasolines having similar volatility characteristics.

5.7 Water Tolerance:

5.7.1 The term water tolerance is used to indicate the ability of a gasoline-oxygenate blend to dissolve water without phase separation. This may not be a problem with gasoline-ether blends, but it is of primary concern for alcohol-containing blends, as blends of gasoline with low-molecular weight alcohols generally will dissolve about 0.1 to 0.7 mass % of water under normal conditions, depending on the nature and amount of the alcohol(s) used, the specific hydrocarbons present, and the temperature of the blend. When blends are exposed to a greater amount of water than they can dissolve, they separate into an alcohol-rich aqueous phase, the volume of which can be significantly greater than that of the additional water, and an alcohol-poor hydrocarbon phase. As the aqueous phase can be highly corrosive to many metals and the engine cannot operate on it, such separation is very undesirable. Blends containing low-molecular weight alcohols are generally hygroscopic and can eventually absorb enough moisture from ambient air to cause separation. The problem of phase separation can usually be avoided if the fuels are sufficiently water-free initially and care is taken during distribution to prevent contact with water. To help ensure this, gasoline-alcohol blends shall be tested at the lowest temperatures to which they can be subjected, dependent on the time and place of intended use, as indicated in Table 13. The values in Table 13 are the 10th percentile 6-h minimum temperatures, with each reading specifically defined as the highest temperature of the six coldest consecutive hourly temperature readings of a 24-h day. For April through September (and occasionally October, and year-round for Hawaii), Table 13 specifies a minimum phase separation temperature of 10°C (50°F), even though the 10th percentile 6-h minimum temperature can be higher. Use of this temperature limit also reduces the risk of separation of the fuel in storage tanks where temperatures may be lower than ambient.

NOTE 5—The values in Table 13 are taken from the U.S. Army Belvoir Research Development and Engineering Center's Report No. 316, entitled "A Predictive Study for Defining Limiting Temperatures and Their

TABLE 4 Schedule of Seasonal and Geographical Volatility Classes^a

NOTE 1—This schedule, subject to agreement between purchaser and seller, denotes the volatility properties of the fuel at the time and place of bulk delivery to the fuel dispensing facilities for the end user. For Sept. 16 through April 30 (the time period not covered by EPA Phase II vapor pressure requirements), volatility properties for the previous month or the current month are acceptable for the end user from the 1st through the 15th day of the month. From the 16th day through the end of the month, volatility properties of the fuel delivered to the end user shall meet the requirements of the specified class(es). To ensure compliance with EPA Phase II vapor pressure requirements, vapor pressure for finished gasoline tankage at refineries, importers, pipelines, and terminals during May and for the entire distribution system, including retail stations, from June 1 to Sept. 15 shall meet only the current month's class. Shipments should anticipate this schedule.

NOTE 2—Where alternative classes are listed, either class or intermediate classes are acceptable; the option shall be exercised by the seller.

NOTE 3—See Appendix X2 of Research Report: D02-1347¹⁵ for detailed description of areas. Contact EPA for the latest information on areas requiring reformulated fuel.

State	Jan.	Feb.	Mar.	Apr.	May ^a	June	July	Aug.	Sept. 1-15	Sept. 16-30	Oct.	Nov.	Dec.
Alabama	D-4	D-4	D-4/C-3	C-3/A-3	A-3 (C-3)	A-3 ^C	A-3 ^C	A-2 ^D	A-2 ^D	A-2/C-3	C-3	C-3/D-4	D-4
Alaska	E-6	E-6	E-6	E-6	E-6/D-4	D-4	D-4	D-4	D-4	D-4/E-6	E-6	E-6	E-6
Arizona: ^b													
N 34° Latitude and E 111° Longitude	D-4	D-4	D-4/C-3	C-3/A-2	A-2 (B-2)	A-1	A-1	A-1	A-2	A-2/B-2	B-2/C-3	C-3/D-4	D-4
Remainder of State	D-4	D-4/C-3	C-3/B-2	B-2/A-2	A-2 (B-2)	A-1 ^F	A-1 ^F	A-1 ^F	A-1 ^D	A-1	A-1/B-2	B-2/C-3	C-3/D-4
Arkansas	E-5/D-4	D-4	D-4/C-3	C-3/A-3	A-3 (C-3)	A-3	A-2	A-2	A-2	A-2/C-3	C-3/D-4	D-4	D-4/E-5
California: ^{b,c}													
North Coast	E-5/D-4	D-4	D-4	D-4/A-3	A-3 (C-3)	A-3 ^C	A-2 ^D	A-2 ^D	A-2 ^D	A-2/B-2	B-2/C-3	C-3/D-4	D-4/E-5
South Coast	D-4	D-4	D-4/C-3	C-3/A-3	A-3 (C-3)	A-2 ^{D,H}	A-2 ^{D,H}	A-2 ^{D,H}	A-2 ^{D,H}	A-2/B-2	B-2/C-3	C-3/D-4	D-4
Southeast	D-4	D-4/C-3	C-3/B-2	B-2/A-2	A-2 (B-2)	A-1 ^F	A-1 ^F	A-1 ^F	A-1 ^F	A-1	A-1/B-2	B-2/C-3	C-3/D-4
Interior	E-5/D-4	D-4	D-4	D-4/A-3	A-3 (C-3)	A-2 ^{D,H}	A-2 ^{D,H}	A-2 ^{D,H}	A-2 ^{D,H}	A-2/B-2	B-2/C-3	C-3/D-4	D-4/E-5
Colorado	E-5	E-5/D-4	D-4/C-3	C-3/A-3	A-3 (C-3)	A-2 ^D	A-2 ^D	A-2 ^D	A-2 ^D	A-2/B-2	B-2/C-3	C-3/D-4	D-4/E-5
Connecticut	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3 ^J	A-3 ^J	A-3 ^J	A-3 ^J	A-3/D-4	D-4	D-4/E-5	E-5
Delaware	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3 ^J	A-3 ^J	A-3 ^J	A-3 ^J	A-3/C-3	C-3/D-4	D-4/E-5	E-5
District of Columbia	E-5	E-5/D-4	D-4	D-4/A-3	A-3 (C-3)	A-3 ^K	A-3 ^K	A-3 ^K	A-3 ^K	A-3/C-3	C-3/D-4	D-4/E-5	E-5
Florida	D-4	D-4	D-4/C-3	C-3/A-3	A-3 (C-3)	A-3 ^C	A-3 ^C	A-3 ^C	A-3 ^C	A-3/C-3	C-3	C-3/D-4	D-4
Georgia: ^b	D-4	D-4	D-4/C-3	C-3/A-3	A-3 (C-3)	A-3 ^C	A-3 ^C	A-2 ^D	A-2 ^D	A-2/C-3	C-3	C-3/D-4	D-4
Hawaii	C-3	C-3	C-3	C-3	C-3	C-3	C-3	C-3	C-3	C-3	C-3	C-3	C-3
Idaho:													
N 46° Latitude	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3	A-2	A-2	A-2	A-2/C-3	C-3/D-4	D-4/E-5	E-5
S 46° Latitude	E-5	E-5/D-4	D-4	D-4/A-3	A-3 (C-3)	A-2	A-2	A-2	A-2	A-2/B-2	B-2/C-3	C-3/D-4	D-4/E-5
Illinois: ^b													
N 40° Latitude	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3 ^J	A-3 ^J	A-3 ^J	A-3 ^J	A-3/C-3	C-3/D-4	D-4/E-5	E-5
S 40° Latitude	E-5	E-5	E-5/D-4	D-4/A-3	A-3 (C-3)	A-3	A-3	A-3	A-3	A-3/C-3	C-3/D-4	D-4	D-4/E-5
Indiana: ^b	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3 ^J	A-3 ^J	A-3 ^J	A-3 ^J	A-3/C-3	C-3/D-4	D-4/E-5	E-5
Iowa	E-5	E-5	E-5/D-4	D-4/A-3	A-3 (C-3)	A-3	A-3	A-3	A-3	A-3/C-3	C-3/D-4	D-4/E-5	E-5
Kansas: ^b	E-5	E-5/D-4	D-4/C-3	C-3/A-3	A-3 (C-3)	A-2 ^D	A-2 ^D	A-2 ^D	A-2 ^D	A-2/B-2	B-2/C-3	C-3/D-4	D-4/E-5
Kentucky	E-5	E-5/D-4	D-4	D-4/A-3	A-3 (C-3)	A-3 ^J	A-3 ^J	A-3 ^J	A-3 ^J	A-3/C-3	C-3/D-4	D-4/E-5	E-5
Louisiana	D-4	D-4	D-4/C-3	C-3/A-3	A-3 (C-3)	A-3 ^C	A-3 ^C	A-2 ^D	A-2 ^D	A-2/C-3	C-3	C-3/D-4	D-4
Maine: ^b	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3	A-3	A-3	A-3	A-3/D-4	D-4	D-4/E-5	E-5
Maryland	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3 ^K	A-3 ^K	A-3 ^K	A-3 ^K	A-3/C-3	C-3/D-4	D-4/E-5	E-5
Massachusetts	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3 ^J	A-3 ^J	A-3 ^J	A-3 ^J	A-3/D-4	D-4	D-4/E-5	E-5
Michigan: ^b	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3	A-3	A-3	A-3	A-3/D-4	D-4	D-4/E-5	E-5
Minnesota	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3	A-3	A-3	A-3	A-3/C-3	C-3/D-4	D-4/E-5	E-5
Mississippi	D-4	D-4	D-4/C-3	C-3/A-3	A-3 (C-3)	A-3	A-3	A-2	A-2	A-2/C-3	C-3	C-3/D-4	D-4
Missouri: ^b	E-5	E-5/D-4	D-4	D-4/A-3	A-3 (C-3)	A-3 ^C	A-2 ^D	A-2 ^D	A-2 ^D	A-2/C-3	C-3/D-4	D-4	D-4/E-5
Montana	E-5	E-5	E-5/D-4	D-4/A-3	A-3 (C-3)	A-2	A-2	A-2	A-2	A-2/C-3	C-3/D-4	D-4/E-5	E-5
Nebraska	E-5	E-5	E-5/D-4	D-4/A-3	A-3 (C-3)	A-2	A-2	A-2	A-2	A-2/B-2	B-2/C-3	C-3/D-4	D-4/E-5
Nevada:													
N 38° Latitude	E-5	E-5/D-4	D-4	D-4/A-3	A-3 (C-3)	A-2 ^D	A-2 ^D	A-2 ^D	A-2 ^D	A-2/B-2	B-2/C-3	C-3/D-4	D-4/E-5
S 38° Latitude	D-4	D-4/C-3	C-3/B-2	B-2/A-2	A-2 (B-2)	A-1	A-1	A-1	A-1	A-1	A-1/B-2	B-2/C-3	C-3/D-4
New Hampshire	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3 ^J	A-3 ^J	A-3 ^J	A-3 ^J	A-3/D-4	D-4	D-4/E-5	E-5
New Jersey	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3 ^J	A-3 ^J	A-3 ^J	A-3 ^J	A-3/D-4	D-4	D-4/E-5	E-5
New Mexico:													
N 34° Latitude	E-5/D-4	D-4	D-4/C-3	C-3/A-2	A-2 (B-2)	A-1	A-1	A-2	A-2	A-2/B-2	B-2/C-3	C-3/D-4	D-4
S 34° Latitude	D-4	D-4/C-3	C-3/B-2	B-2/A-2	A-2 (B-2)	A-1	A-1	A-1	A-1	A-1/B-2	B-2/C-3	C-3/D-4	D-4
New York	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3 ^J	A-3 ^J	A-3 ^J	A-3 ^J	A-3/D-4	D-4	D-4/E-5	E-5
North Carolina	E-5/D-4	D-4	D-4	D-4/A-3	A-3 (C-3)	A-3 ^C	A-3 ^C	A-2 ^D	A-2 ^D	A-2/C-3	C-3/D-4	D-4	D-4/E-5
North Dakota	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3	A-2	A-2	A-2	A-2/C-3	C-3/D-4	D-4/E-5	E-5
Ohio	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3	A-3	A-3	A-3	A-3/C-3	C-3/D-4	D-4/E-5	E-5
Oklahoma	E-5/D-4	D-4	D-4/C-3	C-3/A-3	A-3 (C-3)	A-2	A-2	A-2	A-2	A-2/B-2	B-2/C-3	C-3/D-4	D-4/E-5
Oregon:													
E 122° Longitude	E-5	E-5/D-4	D-4	D-4/A-4	A-4 (D-4)	A-3	A-2	A-2	A-2	A-2/C-3	C-3/D-4	D-4	D-4/E-5
W 122° Longitude	E-5	E-5/D-4	D-4	D-4/A-4	A-4 (D-4)	A-3 ^C	A-3 ^C	A-3 ^C	A-3 ^C	A-3/C-3	C-3/D-4	D-4/E-5	E-5
Pennsylvania: ^b	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3 ^J	A-3 ^J	A-3 ^J	A-3 ^J	A-3/D-4	D-4	D-4/E-5	E-5
Rhode Island	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3 ^J	A-3 ^J	A-3 ^J	A-3 ^J	A-3/D-4	D-4	D-4/E-5	E-5
South Carolina	D-4	D-4	D-4	D-4/A-3	A-3 (C-3)	A-3	A-3 ^J	A-2	A-2	A-2/C-3	C-3/D-4	D-4	D-4
South Dakota	E-5	E-5	E-5/D-4	D-4/A-3	A-3 (C-3)	A-2	A-2	A-2	A-2	A-2/B-2	B-2/C-3	C-3/D-4	D-4/E-5
Tennessee	E-5/D-4	D-4	D-4	D-4/A-3	A-3 (C-3)	A-3 ^C	A-3 ^C	A-2 ^D	A-2 ^D	A-2/C-3	C-3/D-4	D-4	D-4/E-5
Texas: ^b													

TABLE 4 Continued

State	Jan.	Feb.	Mar.	Apr.	May ^a	June	July	Aug.	Sept. 1-15	Sept. 16-30	Oct.	Nov.	Dec.
E 99° Longitude	D-4	D-4	D-4/C-3	C-3/A-3	A-3 (C-3)	A-3 ^{C,K}	A-2 ^{D,H}	A-2 ^{D,H}	A-2 ^{D,H}	A-2/B-2	B-2/C-3	C-3/D-4	D-4
W 99° Longitude	D-4	D-4/C-3	C-3/B-2	B-2/A-2	A-2 (B-2)	A-1 ^F	A-1 ^F	A-1 ^F	A-1 ^F	A-1/B-2	B-2/C-3	C-3/D-4	D-4
Utah	E-5	E-5/D-4	D-4	D-4/A-3	A-3 (C-3)	A-2 ^D	A-2 ^D	A-2 ^D	A-2 ^D	A-2/B-2	B-2/C-3	C-3/D-4	D-4/E-5
Vermont	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3	A-3	A-3	A-3	A-3/D-4	D-4	D-4/E-5	E-5
Virginia	E-5	E-5/D-4	D-4	D-4/A-3	A-3 (C-3)	A-3 ^{C,K}	A-3 ^{C,K}	A-3 ^{C,K}	A-3 ^{C,K}	A-3/C-3	C-3/D-4	D-4/E-5	E-5
Washington:													
E 122° Longitude	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3	A-2	A-2	A-2	A-2/C-3	C-3/D-4	D-4/E-5	E-5
W 122° Longitude	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3	A-3	A-3	A-3	A-3/C-3	C-3/D-4	D-4/E-5	E-5
West Virginia	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3	A-3	A-3	A-3	A-3/C-3	C-3/D-4	D-4/E-5	E-5
Wisconsin	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3 ^J	A-3 ^J	A-3 ^J	A-3 ^J	A-3/C-3	C-3/D-4	D-4/E-5	E-5
Wyoming	E-5	E-5	E-5/D-4	D-4/A-3	A-3 (C-3)	A-2	A-2	A-2	A-2	A-2/B-2	B-2/C-3	C-3/D-4	D-4/E-5

^a For the period May 1 through September 15, the specified vapor pressure classes comply with 1992 U.S. EPA Phase II volatility regulations. Reformulated spark-ignition engine fuel blended to meet the requirements of the EPA "Complex Model" shall also meet the Phase II volatility regulations. EPA regulations (under the Phase II regulations) allow 1.0 psi higher vapor pressure for gasoline-ethanol blends containing 9 to 10 volume % ethanol for the same period, except for fuels blended to meet the "Complex Model" regulations. See Appendix X3 for additional federal volatility regulations.

^b Values in parentheses are permitted for retail stations and other end users.

^c See Table 5 for specific area requirements.

^d See Table 6 for specific area requirements.

^e See Table 12 for specific area requirements.

^f See Table 7 for specific area requirements.

^g Details of State Climatological Division by CARB air basin and county as indicated (Descriptions of the California Air Basins are found in the California Code of Regulations):

California, North Coast—CARB North Coast, Lake County, San Francisco Bay Area, and North Central Coast Air Basins (Alameda, Contra Costa, Del Norte, Humboldt, Lake, Marin, Mendocino, Monterey, Napa, San Benito, San Francisco, San Mateo, Santa Clara, Santa Cruz, Solano, Sonoma, and Trinity Counties and part of Solano County).

California, interior—CARB Northeast Plateau, Sacramento Valley, Mountain Counties, Lake Tahoe, and San Joaquin Valley Air Basins (Amador, Butte, Calaveras, Colusa, El Dorado, Fresno, Glenn, Kings, Lassen, Madera, Mariposa, Merced, Modoc, Nevada, Placer, Plumas, Sacramento, San Joaquin, Shasta, Sierra, Siskiyou, Stanislaus, Sutter, Tehama, Tulare, Tuolumne, Yolo, and Yuba Counties, and parts of Kern and Solano Counties).

California, South Coast—CARB South Central Coast, San Diego, and South Coast Air Basins (Los Angeles, Orange, San Diego, San Luis Obispo, Santa Barbara, and Ventura Counties, and parts of Riverside and San Bernardino Counties).

California, Southeast—CARB Great Basin Valleys, Salton Sea, and Mojave Desert Air Basins (Alpine, Imperial, Inyo, and Mono Counties, and parts of Kern, Los Angeles, Riverside, San Bernardino Counties).

^h See Table 10 for specific requirements.

ⁱ See Table 11 for specific area requirements.

^j See Table 8 for specific area requirements.

^k See Table 9 for specific area requirements.

TABLE 5 Ozone Nonattainment Areas Requiring Volatility Class AA-3

Note—See 40 CFR Part 81.300 for description of the geographic boundary for each area.

Alabama^a—Jefferson and Shelby counties
 California^a—Alameda, Contra Costa, Marin, Monterey, Napa, San Francisco, San Benito, San Mateo, Santa Clara, Santa Cruz, and Solano (part) counties
 Florida—Broward, Dade, Duval, Hillsborough, Palm Beach, and Pinellas counties
 Georgia^a—Cherokee, Clayton, Cobb, Coweta, DeKalb, Douglas, Fayette, Forsyth, Fulton, Gwinnett, Henry, Paulding, and Rockdale counties
 Louisiana—Ascension, Beauregard, Calcasieu, East Baton Rouge, Grant, Iberville, Jefferson, Lafayette, Lafourche, Livingston, Orleans, Point Coupee, Saint Bernard, Saint Charles, Saint James, Saint Mary, and West Baton Rouge parishes
 Missouri—Franklin, Jefferson, Saint Charles, and Saint Louis counties; and the city of St. Louis
 North Carolina—Davidson, Davie (part), Durham, Forsyth, Gaston, Granville (part), Guilford, Mecklenburg, and Wake counties
 Oregon—Clackamas (part), Marion (part), Multnomah (part), Polk (part), and Washington (part) counties
 Tennessee—Davidson, Rutherford, Shelby, Sumner, Williamson, and Wilson counties
 Texas—Hardin, Jefferson, Orange, and Victoria counties
 Virginia—Smyth County (part)

^a See Table 12 for local vapor pressure limits.

Application in Petroleum Product Specifications." This can be obtained as Publication AD756-420 from the National Technical Information Service, Springfield, VA 22151.

5.7.2 The water tolerance test procedure consists of cooling gasoline-alcohol blends under specified conditions to the

TABLE 6 Ozone Nonattainment Areas Requiring Volatility Class AA-2

Note—See 40 CFR Part 81.300 for description of the geographic boundary for each area.

Alabama^a—Jefferson and Shelby counties
 Arizona^a—Maricopa County
 California^a—Alameda, Butte, Contra Costa, Fresno, Kern (part), Kings, Madera, Marin, Merced, Monterey, Napa, San Benito, San Francisco, San Joaquin, San Mateo, Santa Barbara, Santa Clara, Santa Cruz, Stanislaus, Tulare, and Yuba counties
 Colorado—Adams, Arapahoe, Boulder, Denver, Douglas, and Greeley counties
 Georgia^a—Cherokee, Clayton, Cobb, Coweta, DeKalb, Douglas, Fayette, Forsyth, Fulton, Gwinnett, Henry, Paulding, and Rockdale counties
 Kansas^a—Johnson and Wyandotte counties
 Louisiana—Ascension, Beauregard, Calcasieu, East Baton Rouge, Grant, Iberville, Jefferson, Lafayette, Lafourche, Livingston, Orleans, Point Coupee, Saint Bernard, Saint Charles, Saint James, Saint Mary, and West Baton Rouge parishes
 Missouri—Franklin, Jefferson, Saint Charles, and Saint Louis counties; and the city of St. Louis
 Nevada—Washoe County
 North Carolina—Davidson, Davie (part), Durham, Forsyth, Gaston, Granville (part), Guilford, Mecklenburg, and Wake counties
 Tennessee—Davidson, Rutherford, Shelby, Sumner, Williamson, and Wilson counties
 Texas—Hardin, Jefferson, Orange, and Victoria counties
 Utah—Davis and Salt Lake counties

^a See Table 12 for local vapor pressure limits.

appropriate temperature listed in Table 13. It is important to note that when cooling to a low temperature, some gasoline-alcohol blends can take on a hazy appearance. This haze must

TABLE 7 Ozone Nonattainment Areas Requiring Volatility Class AA-1

Note—See 40 CFR Part 81.300 for description of the geographic boundary for each area.

Arizona^A—Maricopa County
California^A—Imperial and Kern (part) counties
Texas^A—El Paso County

^A See Table 12 for local vapor pressure limits.

TABLE 8 Federal RFG Areas Requiring Volatility Class A-3

Note 1—See 40 CFR Part 81.300 for description of the geographic boundary for each area.

Note 2—No waiver for gasoline-ethanol blends.

Connecticut—All counties
Delaware—All counties
Illinois^A—Cook, Du Page, Grundy (part), Kane, Kendall (part), Lake, McHenry, and Will counties
Indiana^A—Lake and Porter counties
Kentucky—Boone, Bullitt (part), Campbell, Jefferson, Kenton, and Oldham (part) counties
Maryland—Cecil County
Massachusetts—All counties
New Hampshire—Hillsborough, Merrimack, Rockingham, and Strafford counties
New Jersey—All counties
New York—Bronx, Dutchess, Essex (part), Kings, Nassau, New York, Orange, Putnam, Queens, Richmond, Rockland, Suffolk, and Westchester counties
Pennsylvania—Bucks, Chester, Delaware, Montgomery, and Philadelphia counties
Rhode Island—All counties
Wisconsin—Kenosha, Milwaukee, Ozaukee, Racine, Washington, and Waukesha counties

^A See Table 12 for local vapor pressure limits.

TABLE 9 Federal RFG Areas Requiring Volatility Class AA-3

Note 1—See 40 CFR Part 81.300 for description of the geographic boundary for each area.

Note 2—No waiver for gasoline-ethanol blends.

District of Columbia
Maryland—Anne Arundel, Baltimore, Calvert, Carroll, Charles, Frederick, Harford, Howard, Kent, Montgomery, Prince George's, and Queen Anne's counties
Texas—Brazoria, Chambers, Collin, Dallas, Denton, Fort Bend, Galveston, Harris, Liberty, Montgomery, Tarrant, and Waller counties
Virginia—Arlington, Charles City, Chesterfield, Fairfax, Hanover, Henrico, James City, Loudoun, Prince William, Stafford, and York counties and independent cities of Alexandria, Chesapeake, Colonial Heights, Fairfax, Falls Church, Hampton, Hopewell, Manassas, Manassas Park, Newport News, Norfolk, Poquoson, Portsmouth, Richmond, Suffolk, Virginia Beach, and Williamsburg

be carefully distinguished from the phase separation test criterion described in Test Method D 6422 and must not be considered grounds for rejection of the fuel. This test must not be confused with that described in Section 6, which is conducted at 21°C (70°F) or above, and for which the appearance of haze is proper grounds for rejection.

5.8 Deposit control additives are added to fuel to help keep carburetors, fuel injectors, and intake valves clean. Deposit control additives are required to be certified by the EPA as summarized in X3.5. Each additive is certified for use at a lowest additive concentration (LAC), which is the lowest level certified to be effective in preventing deposit formation. All parties who blend deposit control additives into fuel must complete mandatory volume additive reconciliation (VAR)

TABLE 10 Federal RFG Areas Requiring Volatility Class AA-2

Note 1—See 40 CFR Part 81.305 for description of the geographic boundary for each area.

Note 2—No waiver for gasoline-ethanol blends.

California^A—El Dorado (part), Los Angeles, Orange, Placer (part), Riverside (part), Sacramento, San Bernardino (part), San Diego, Solano (part), Sutter (part), Ventura, and Yolo Counties
Texas—Brazoria, Chambers, Collin, Dallas, Denton, Fort Bend, Galveston, Harris, Liberty, Montgomery, Tarrant, and Waller counties

^A See Table 12 for local vapor pressure limits.

TABLE 11 Federal RFG Area Requiring Volatility Class AA-1

Note 1—See 40 CFR Part 81.300 for description of the geographic boundary for each area.

Note 2—No waiver for gasoline-ethanol blends.

California^A—Los Angeles (part), Riverside (part), and San Bernardino (part) counties

^A See Table 12 for local vapor pressure limits.

accounting to establish that the product was additized at a concentration that was at least equal to the LAC.

6. Workmanship

6.1 The finished fuel shall be visually free of undissolved water, sediment, and suspended matter; it shall be clear and bright at the ambient temperature or 21°C (70°F), whichever is higher.

6.2 Fuel to be used in this test shall not be cooled below about 15°C (59°F) or its temperature at the time the sample was taken, whichever is lower, as cooling of gasoline-oxygenate blends can produce changes in appearance that are not reversed on rewarming.

6.3 The finished fuel shall also be free of any adulterant or contaminant that may render the fuel unacceptable for its commonly used applications.

7. Test Methods

7.1 The requirements of this specification shall be determined in accordance with the methods listed below. Refer to the listed test methods to determine applicability or required modifications for use with gasoline-oxygenate blends.

7.1.1 *Distillation*—Test Method D 86.

7.1.2 *Vapor-Liquid Ratio*—Test Method D 2533 has procedures for determining vapor-liquid (V/L) ratios for both gasoline and gasoline-oxygenate blends. Because some oxygenates are miscible with the glycerin used in one procedure, another procedure using mercury as the confining fluid is provided for gasoline-oxygenate blends. Either procedure may be used to determine V/L for gasoline. Test Method D 5188 is an evacuated chamber method for determining temperatures for vapor-liquid ratios between 8 to 1 and 75 to 1. It may be used for gasoline and gasoline-oxygenate blends.

7.1.3 *Vapor Pressure*—Test Methods D 4953, D 5190, D 5191, or D 5482.

7.1.4 *Corrosion, for Copper*—Test Method D 130, 3 h at 50°C (122°F).

7.1.5 *Solvent-Washed Gum Content*—Test Method D 381, air jet apparatus.

TABLE 12 Federal Approved State Implementation Plan Areas Requiring More Restrictive Maximum Vapor Pressure Limits

NOTE—Some areas are awaiting official EPA approval for the more restrictive local vapor pressure limits.

Alabama—Jefferson and Shelby counties—48.2 kPa (7.0 psi) max June 1 - Sept. 15
Arizona—Maricopa County—48.2 kPa (7.0 psi) max May 31 - Sept. 30, 62.0 kPa (9.0 psi) max Oct. 1 - Mar. 31
California—48.26 kPa (7.00 psi) max April 1, May 1, or June 1 - Sept. 30 or Oct. 31 depending on air basin
Georgia—Banks, Barrow, Bartow, Butts, Carroll, Chattooga, Cherokee, Clarke, Clayton, Cobb, Coweta, Dawson, DeKalb, Douglas, Fayette, Floyd, Forsyth, Fulton, Gwinnett, Hall, Haralson, Heard, Henry, Jackson, Jasper, Jones, Lamar, Lumpkin, Madison, Meriwether, Monroe, Morgan, Newton, Oconee, Paulding, Pickens, Pike, Polk, Putnam, Rockdale, Spalding, Troup, Upson, and Walton counties—48.2 kPa (7.0 psi) max June 1 - Sept. 15 ^A
Illinois—Madison, Monroe, and Saint Clair Counties area - 49.6 kPa (7.2 psi) max June 1 - Sept. 15 ^A
Indiana—Clark and Floyd counties area - 53.8 kPa (7.8 psi) max May 1 terminal/June 1 retail - Sept. 15 ^A
Kansas—Johnson and Wyandotte counties—48.2 kPa (7.0 psi) max June 1 - Sept. 15 ^A
Maine—Androscoggin, Cumberland, Kennebec, Knox, Lincoln, Sagadahoc, and York Counties—53.8 kPa (7.8 psi) max May 1-Sept. 15
Michigan—Livingston, Macomb, Monroe, Oakland, Saint Clair, Washtenaw, and Wayne counties—53.8 kPa (7.8 psi) max June 1 - Sept. 15
Missouri—Clay, Jackson, and Platte counties—48.2 kPa (7.0 psi) max June 1 - Sept. 15 ^A
Pennsylvania—Allegheny, Armstrong, Beaver, Butler, Fayette, Washington, and Westmoreland counties—53.8 kPa (7.8 psi) max June 1 - Sept. 15
Texas—El Paso County—48.2 kPa (7.0 psi) max May 1 terminal/June 1 retail - Sept. 15
Texas—Anderson, Angelina, Aransas, Atascosa, Austin, Bastrop, Bee, Bell, Bexar, Bosque, Bowie, Brazos, Burleson, Caldwell, Calhoun, Camp, Cass, Cherokee, Colorado, Comal, Cooke, Coryell, De Witt, Delta, Ellis, Falls, Fannin, Fayette, Franklin, Freestone, Goliad, Gonzales, Grayson, Gregg, Grimes, Guadalupe, Harrison, Hays, Henderson, Hill, Hood, Hopkins, Houston, Hunt, Jackson, Jasper, Johnson, Karnes, Kaufman, Lamar, Lavaca, Lee, Leon, Lime-stone, Live Oak, Madison, Marion, Matagorda, McLennan, Milam, Morris, Ne-cogdoches, Nararero, Newton, Nueces, Panola, Parker, Polk, Rains, Red River, Refugio, Robertson, Rockwall, Rusk, Sabine, San Jacinto, San Patricio, San Augustine, Shelby, Smith, Somervell, Titus, Travis, Trinity, Tyler, Upshur, Van-Zandt, Victoria, Walker, Washington, Wharton, Williamson, Wilson, Wise, and Wood counties—53.8 kPa (7.8 psi) max May 1 terminal/June 1 retail - October 1

^A A 1.0 psi higher vapor pressure is allowed for gasoline-ethanol blends containing 9 to 10 volume % ethanol.

7.1.6 Sulfur—Test Methods D 1266, D 2622, D 3120, or D 5453. With Test Method D 3120, fuels with sulfur content greater than 100 ppm (0.0100 mass %) must be diluted with isooctane. The dilution of the sample may result in a loss of precision. Test Method D 3120 cannot be used when the lead concentration is greater than 0.4 g/L (1.4 g/U.S. gal).

7.1.7 Lead—Test Methods D 3341 or D 5059 (Test Methods A or B). For lead levels below 0.03 g/L (0.1 g/U.S. gal), use Test Methods D 3237 or D 5059 (Test Method C).

7.1.8 Oxidation Stability—Test Method D 525.

7.1.9 Oxygenate Detection—Test Methods D 4815, D 5599, or D 5845. These test methods are designed for the quantitative determination of methyl *tert*-butyl ether (MTBE), ethyl *tert*-butyl ether (ETBE), *tert*-amyl methyl ether (TAME), diisopropyl ether (DIPE), methyl alcohol, ethyl alcohol, and *tert*-butyl alcohol. In addition, Test Methods D 4815 and D 5599 are designed for the quantitative determination of *n*-propyl alcohol, isopropyl alcohol, *n*-butyl alcohol, *sec*-butyl alcohol, isobutyl alcohol, and *tert*-pentyl alcohol. Results for all of these test methods are reported in mass %. Test Method D 4815

includes procedures for calculating oxygenate concentration in volume % and mass oxygen content using the mass % oxygenate results.

7.1.10 Water Tolerance—See Test Method D 6422.

8. Precision and Bias ⁷

8.1 The precision of each required test method for the properties specified is included in the standard applicable to each method, with the exception of Driveability Index. In many cases, the precision applicable to gasoline-oxygenate blends has not been established yet.

8.2 Precision and Bias of Driveability Index (DI):

8.2.1 The following statements apply to the precision and bias of DI, which is a derived quantity not addressed in any other standard.⁷

8.2.2 The precision of DI is a function of the individual precisions of the 10 %, 50 %, and 90 % evaporated temperatures from Test Method D 86. The precisions of these percent evaporated temperatures vary for different apparatuses (manual or automatic), for fuels of different volatilities (for example, above and below 65.5 kPa (9.5 psi) vapor pressure) and with different distillation curve slopes.

8.2.3 Repeatability—The difference between two successive DI determinations using Test Method D 86 results, where the two test results were obtained by one operator with the same apparatus under constant operating conditions on identical test material, would in the long run, in normal and correct operation of the test method, exceed 9°C (17°F) derived units in only one case in twenty.

8.2.4 The repeatability value was calculated using the precision data from Test Method D 86 and average distillation characteristics from the 1994 through 1998 ASTM Committee D02 Interlaboratory Crosscheck Program for Motor Gasoline and from the 1997 and 1998 ASTM Committee D02 Interlaboratory Crosscheck Program for Reformulated Gasoline.

8.2.5 Reproducibility—The difference between two single and independent DI determinations using Test Method D 86 results, where the two test results were obtained by different operators in different laboratories on identical test material, would in the long run, in normal and correct operation of the test method, exceed 27°C (48°F) derived units in only one case in twenty.

8.2.6 The reproducibility values were determined directly using the distillation data from each laboratory participating in cooperative programs to calculate DI. The data used to calculate DI were available from the 1994 through 1998 ASTM Committee D02 Interlaboratory Crosscheck Program for Motor Gasoline, the 1997 and 1998 ASTM Committee D02 Interlaboratory Crosscheck Program for Reformulated Gasoline, the Auto/Oil Air Quality Improvement Research Program, the Auto/Oil AAMA Gasoline Inspections Program, and the 1995 to 1996 CRC volatility program.

8.2.7 Bias—Since there is no acceptable reference material suitable for determining bias for DI, bias has not been determined.

⁷ Supporting data (calculations) have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1468.

TABLE 13 Maximum Temperature for Phase Separation, °C^a

Temperature Conversion °F = (°C × 1.8) + 32°												
State	Jan.	Feb.	March	April	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
Alabama	-4.	-3.	0.	5.	10.	10.	10.	10.	10.	6.	0.	-4.
^b Alaska:												
Southern Region	-27.	-26.	-23.	-11.	1.	7.	9.	7.	1.	-9.	-19.	-23.
South Mainland	-41.	-39.	-31.	-14.	-1.	7.	9.	5.	-2.	-18.	-32.	-41.
N of 62° Latitude												
Arizona:												
N of 34° Latitude	-11.	-7.	-7.	-2.	2.	6.	10.	10.	8.	1.	-6.	-9.
S of 34° Latitude	-2.	-1.	2.	-7.	10.	10.	10.	10.	10.	9.	2.	-1.
Arkansas	-9.	-8.	-2.	6.	10.	10.	10.	10.	10.	4.	-2.	-6.
^c California												
North Coast	-2.	0.	1.	4.	5.	8.	9.	9.	8.	6.	2.	-2.
South Coast	-2.	-1.	2.	4.	7.	9.	10.	10.	9.	6.	1.	-2.
Southeast	-7.	-3.	-1.	3.	8.	10.	10.	10.	9.	4.	-3.	-6.
Interior	-4.	-3.	-3.	-1.	3.	9.	10.	10.	10.	6.	0.	-2.
Colorado:												
E of 105° Longitude	-14.	-12.	-9.	-3.	4.	10.	10.	10.	7.	1.	-8.	-11.
W of 105° Longitude	-24.	-20.	-12.	-6.	-1.	4.	8.	6.	1.	-6.	-14.	-21.
Connecticut	-14.	-13.	-8.	-1.	5.	10.	10.	10.	7.	1.	-4.	-12.
Delaware	-9.	-8.	-3.	0.	8.	10.	10.	10.	10.	4.	-1.	-8.
District Columbia	-8.	-7.	-3.	3.	9.	10.	10.	10.	10.	5.	0.	-7.
Florida:												
N of 29° Latitude	-1.	1.	4.	9.	10.	10.	10.	10.	10.	9.	3.	-1.
S of 29° Latitude	4.	7.	8.	10.	10.	10.	10.	10.	10.	10.	9.	5.
Georgia	-5.	-2.	1.	6.	10.	10.	10.	10.	10.	6.	0.	-3.
Hawaii	10.	10.	10.	10.	10.	10.	10.	10.	10.	10.	10.	10.
Idaho	-17.	-16.	-11.	-3.	-5.	4.	10.	9.	3.	-2.	-11.	-15.
Illinois:												
N of 40° Latitude	-18.	-16.	-9.	-1.	4.	10.	10.	10.	7.	1.	-7.	-16.
S of 40° Latitude	-15.	-12.	-7.	1.	7.	10.	10.	10.	9.	3.	-8.	-13.
Indiana	-16.	-13.	-7.	-1.	4.	10.	10.	10.	7.	1.	-6.	-14.
Iowa	-23.	-19.	-13.	-3.	4.	10.	10.	10.	6.	0.	-12.	-20.
Kansas	-17.	-12.	-9.	-3.	5.	10.	10.	10.	7.	0.	-8.	-13.
Kentucky	-12.	-9.	-4.	1.	8.	10.	10.	10.	9.	3.	-4.	-11.
Louisiana	-3.	0.	3.	8.	10.	10.	10.	10.	10.	7.	2.	-1.
Maine	-24.	-22.	-16.	-4.	1.	7.	10.	8.	3.	-2.	-8.	-20.
Maryland	-9.	-8.	-3.	3.	9.	10.	10.	10.	10.	4.	-2.	-8.
Massachusetts	-15.	-14.	-7.	-1.	4.	10.	10.	10.	6.	0.	-4.	-13.
^d Michigan:												
Lower Michigan	-18.	-17.	-12.	-3.	1.	7.	10.	9.	5.	0.	-6.	-14.
Upper Michigan	-21.	-20.	-15.	-8.	-1.	6.	9.	9.	4.	-1.	-9.	-18.
Minnesota	-31.	-28.	-20.	-7.	0.	6.	10.	8.	1.	-3.	-16.	-28.
Mississippi	-3.	-1.	2.	7.	10.	10.	10.	10.	10.	7.	1.	-3.
Missouri	-14.	-11.	-6.	1.	8.	10.	10.	10.	10.	3.	-5.	-12.
Montana	-28.	-24.	-19.	-6.	1.	5.	9.	8.	1.	-5.	-17.	-23.
Nebraska	-19.	-14.	-11.	-3.	4.	9.	10.	10.	5.	-2.	-10.	-16.
Nevada:												
N of 38° Latitude	-18.	-13.	-8.	-3.	1.	5.	9.	7.	2.	-3.	-11.	-14.
S of 38° Latitude	-9.	-5.	-1.	1.	9.	10.	10.	10.	10.	4.	-3.	-6.
New Hampshire	-18.	-17.	-9.	-2.	3.	9.	10.	9.	3.	-1.	-6.	-16.
New Jersey	-10.	-9.	-4.	2.	7.	10.	10.	10.	10.	4.	-1.	-8.
New Mexico:												
N of 34° Latitude	-14.	-11.	-7.	-2.	1.	7.	10.	10.	7.	1.	-8.	-12.
S of 34° Latitude	-7.	-5.	-1.	6.	10.	10.	10.	10.	10.	7.	-2.	-5.
New York:												
N of 42° Latitude	-21.	-20.	-13.	-3.	2.	9.	10.	10.	4.	-1.	-6.	-18.
S of 42° Latitude	-13.	-13.	-7.	1.	6.	10.	10.	10.	8.	2.	-3.	-12.
North Carolina	-9.	-7.	-3.	1.	7.	10.	10.	10.	8.	1.	-5.	-8.
North Dakota	-29.	-27.	-11.	-8.	1.	8.	10.	10.	3.	-2.	-17.	-24.
Ohio	-14.	-13.	-8.	-2.	6.	10.	10.	10.	7.	1.	-5.	-13.
Oklahoma	-12.	-6.	-5.	1.	7.	10.	10.	10.	10.	4.	-4.	-9.
Oregon:												
E of 122° Longitude	-17.	-12.	-6.	-3.	0.	4.	6.	6.	2.	-3.	-8.	-12.
W of 122° Longitude	-5.	-3.	-1.	2.	5.	8.	10.	10.	7.	2.	-3.	-3.
Pennsylvania:												
N of 41° Latitude	-17.	-19.	-13.	-4.	1.	6.	9.	8.	2.	-1.	-6.	-16.
S of 41° Latitude	-13.	-14.	-9.	-1.	5.	10.	10.	10.	7.	2.	-4.	-12.
Rhode Island	-11.	-11.	-5.	1.	6.	10.	10.	10.	8.	3.	-2.	-10.
South Carolina	-3.	-2.	0.	6.	10.	10.	10.	10.	10.	7.	1.	-3.
South Dakota	-24.	-21.	-16.	-4.	3.	10.	10.	10.	4.	-2.	-12.	-21.
Tennessee	-9.	-7.	-3.	2.	9.	10.	10.	10.	10.	2.	-3.	-8.
Texas:												
N of 31° Latitude	-11.	-8.	-4.	2.	8.	10.	10.	10.	10.	5.	-3.	-7.

TABLE 13 Continued

Temperature Conversion °F = (°C × 1.8) + 32°												
State	Jan.	Feb.	March	April	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
S of 31° Latitude	-1.	1.	4.	10.	10.	10.	10.	10.	10.	10.	3.	1.
Utah	-15.	-11.	-7.	-2.	2.	8.	10.	10.	7.	2.	-11.	-12.
Vermont	-20.	-21.	-12.	-2.	2.	9.	10.	10.	5.	0.	-6.	-17.
Virginia	-8.	-7.	-3.	3.	9.	10.	10.	10.	10.	4.	-2.	-7.
Washington:												
E of 122° Longitude	-13.	-8.	-3.	1.	4.	7.	10.	10.	7.	1.	-5.	-7.
W of 122° Longitude	-6.	-2.	-2.	1.	4.	7.	9.	9.	6.	2.	-2.	-2.
West Virginia	-13.	-12.	-7.	-2.	4.	9.	10.	10.	5.	-2.	-7.	-12.
Wisconsin	-25.	-21.	-15.	-3.	3.	8.	10.	10.	5.	-1.	-11.	-21.
Wyoming	-23.	-17.	-14.	-6.	0.	5.	10.	10.	3.	-2.	-13.	-16.

^a A maximum phase separation temperature of 10°C (50°F) is specified, even if the 6-h 10th percentile minimum temperature for the area and month can be higher.
^b The designated areas of Alaska are divided as follows: *Southern Region*—The Aleutians, Kodiak Island, the coastal strip East of Longitude 141°, and the Alaskan Peninsula South of Latitude 62°.

South Mainland—The portion of Alaska South of Latitude 62°, except the Southern Region.

North of Latitude 62°—The specification test temperature must be agreed between the vendor and purchaser having regard to equipment design, expected weather conditions, and other relevant factors.

^c The designated areas of California are divided by county as follows: *North Coast*—Alameda, Contra Costa, Del Norte, Humboldt, Lake, Marin, Mendocino, Monterey, Napa, San Benito, San Francisco, San Mateo, Santa Clara, Santa Cruz, Solano, Sonoma, Trinity.

Interior—Lassen, Modoc, Plumas, Sierra, Siskiyou, Alpine, Amador, Butte, Calaveras, Colusa, El Dorado, Fresno, Glenn, Kern (excepting that portion lying east of the Los Angeles County Aqueduct, Kings, Madera, Mariposa, Merced, Placer, Sacramento, San Joaquin, Shasta, Stanislaus, Sutter, Tehama, Tulare, Tuolumne, Yolo, Yuba, Nevada.

South Coast—Orange, San Diego, San Luis Obispo, Santa Barbara, Ventura, Los Angeles (except that portion lying north of the San Gabriel Mountain range and east of the Los Angeles County Aqueduct).

Southeast—Imperial, Riverside, San Bernardino, Los Angeles (that portion lying north of the San Gabriel Mountain range and east of the Los Angeles County Aqueduct), Mono, Inyo, Kern (that portion lying east of the Los Angeles County Aqueduct).

^d The designated areas of Michigan are divided as follows: *Lower Michigan*—That portion of the state lying East of Lake Michigan.

Upper Michigan—That portion of the state lying North of Wisconsin and of Lake Michigan.

9. Keywords

9.1 alcohol; antiknock index; automotive fuel; automotive gasoline; automotive spark-ignition engine fuel; copper strip corrosion; corrosion; distillation; driveability; Driveability Index; EPA regulations; ethanol; ether; fuel; gasoline; gasoline-alcohol blend; gasoline-ethanol blend; gasoline-ether blend;

gasoline-oxygenate blend; induction period; lead; leaded fuel; methanol; MTBE; octane number; octane requirement; oxidation stability; oxygenate; oxygenate detection; phase separation; phosphorous; solvent-washed gum; sulfur; $T_{V/L} = 20$; unleaded fuel; vapor-liquid ratio; vapor lock; vapor pressure; volatility; water tolerance

APPENDICES

(Nonmandatory Information)

X1. SIGNIFICANCE OF ASTM SPECIFICATION FOR AUTOMOTIVE SPARK-IGNITION ENGINE FUEL

X1.1 General

X1.1.1 Antiknock rating and volatility define the general characteristics of automotive spark-ignition engine fuel. Other characteristics relate to the following: limiting the concentration of undesirable components so that they will not adversely affect engine performance and ensuring the stability of fuel as well as its compatibility with materials used in engines and their fuel systems.

X1.1.2 Fuel for spark-ignition engines is a complex mixture composed of relatively volatile hydrocarbons that vary widely in their physical and chemical properties and may contain oxygenates. Fuel is exposed to a wide variety of mechanical, physical, and chemical environments. Thus, the properties of fuel must be balanced to give satisfactory engine performance over an extremely wide range of operating conditions. The prevailing standards for fuel represent compromises among the numerous quality and performance requirements. This ASTM specification is established on the basis of the broad experience

and close cooperation of producers of fuel, manufacturers of automotive equipment, and users of both.

X1.2 Engine Knock

X1.2.1 The fuel-air mixture in the cylinder of a spark-ignition engine will, under certain conditions, autoignite in localized areas ahead of the flame front that is progressing from the spark. This is engine spark knock which can cause a ping that may be audible to the customer.

X1.2.2 The antiknock rating of a fuel is a measure of its resistance to knock. The antiknock requirement of an engine depends on engine design and operation, as well as atmospheric conditions. Fuel with an antiknock rating higher than that required for knock-free operation does not improve performance.

X1.2.3 A decrease in antiknock rating may cause vehicle performance loss. However, vehicles equipped with knock limiters can show a performance improvement as the antiknock

quality of the fuel is increased in the range between customer-audible knock and knock-free operation. The loss of power and the damage to an automotive engine due to knocking are generally not significant until the knock intensity becomes very severe. Heavy and prolonged knocking may cause power loss and damage to the engine.

X1.3 Laboratory Octane Number

X1.3.1 The two recognized laboratory engine test methods for determining the antiknock rating of fuels are the Research method (Test Methods D 2699 or D 2885) and the Motor method (Test Methods D 2700 or D 2885). The following paragraphs define the two methods and describe their significance as applied to various equipment and operating conditions.

X1.3.2 Research octane number is determined by a method that measures fuel antiknock level in a single-cylinder engine under mild operating conditions; namely, at a moderate inlet mixture temperature and a low engine speed. Research octane number tends to indicate fuel antiknock performance in engines at wide-open throttle and low-to-medium engine speeds.

X1.3.3 Motor octane number is determined by a method that measures fuel antiknock level in a single-cylinder engine under more severe operating conditions than those employed in the Research method; namely, at a higher inlet mixture temperature and at a higher engine speed. It indicates fuel antiknock performance in engines operating at wide-open throttle and high engine speeds. Also, Motor octane number tends to indicate fuel antiknock performance under part-throttle, road-load conditions.

X1.4 Road Octane Number

X1.4.1 The road octane of a fuel is the measure of its ability to resist knock in customers' vehicles, and is ultimately of more importance than laboratory octane numbers. Since road octanes are difficult to measure and interpret, the industry has agreed to use ASTM laboratory engine tests to estimate the road octane performance of spark-ignition engine fuel in vehicles.

X1.4.2 The antiknock index (AKI) is the arithmetic average of the Research octane number (RON) and Motor octane number (MON):

$$AKI = (RON + MON)/2 \quad (X1.1)$$

This value is called by a variety of names, in addition to antiknock index, including:

- Octane rating
- Posted octane
- (R + M)/2 octane

X1.4.3 The AKI is posted on retail gasoline dispensing pumps in the United States and is referred to in car owners' manuals. The AKI is also required for certification at each wholesale fuel transfer and is referred to in United States federal law as "Octane Rating."⁸

⁸ Details of this regulation can be found in Code of Federal Regulations Title 16, Chapter 1, Subchapter C, part 306 (16 CFR306), U.S. Government Printing Office, Superintendent of Documents, Washington DC 20402.

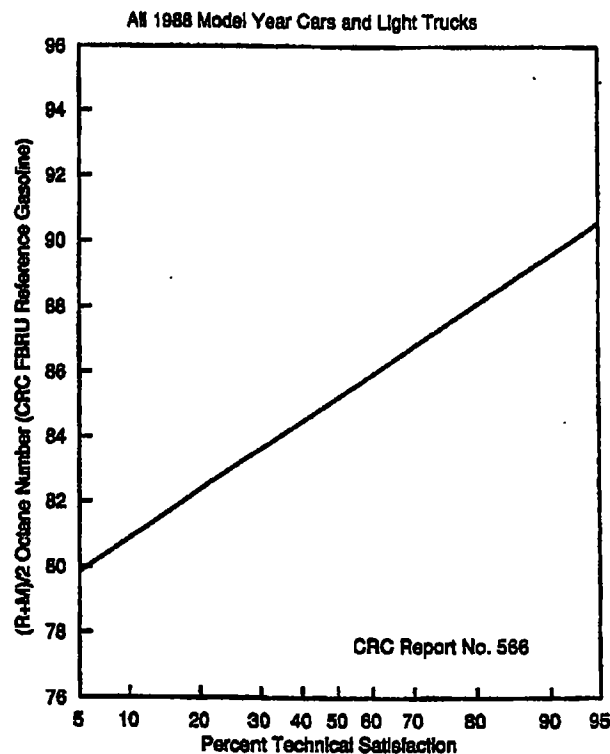


FIG. X1.1 An Example of the Statistical Distribution of Vehicle Antiknock Requirements

X1.4.4 The most extensive data base that relates the laboratory engine test methods for Research and Motor octane to actual field performance of fuel in vehicles is the annual Coordinating Research Council (CRC)⁹ Octane Number Requirement Survey conducted for new light-duty vehicles. Analysis of these data shows that the antiknock performance of a fuel in some vehicles may correlate best with Research octane number, while in others, it may correlate best with Motor octane number. These correlations also differ from model year to model year or from vehicle population to vehicle population, reflecting changes in engine designs over the years.

X1.4.5 The antiknock index of a fuel approximates the CRC road octane ratings for many vehicles. However, the user must also be guided by experience as to which fuel is most appropriate for an individual vehicle. The antiknock index formula is reviewed periodically and may have to be adjusted in the future as engines and fuels continue to evolve. The present $(RON + MON)/2$ formula is an estimate and is not an absolute measure of fuel antiknock performance in general or in any specific vehicle.

X1.4.6 Car antiknock requirements vary, even within a single model, so the statistical distribution of the octane needs of any car population are usually shown in graphical form, as shown in Fig. X1.1. As antiknock index increases, larger and larger fractions of the car population in question will be free of

⁹ Coordinating Research Council, Inc., 3650 Mansell Rd., Ste. 140, Alpharetta, GA 30022-8246.

TABLE X1.1 Automotive Spark-Ignition Engine Fuel Antiknock Indexes in Current Practice

Unleaded Fuel ^A (for vehicles that can or must use unleaded fuel)	
Antiknock Index ^{B,C,D,E} (RON + MON)/2	Application
87	Designed to meet antiknock requirements of most 1971 and later model vehicles
89	Satisfies vehicles with somewhat higher antiknock requirements
91 and above	Satisfies vehicles with high antiknock requirements
Leaded Fuel (for vehicles that can or must use leaded fuel)	
Antiknock Index ^{B,C,D,E} (RON + MON)/2	Application
88	For most vehicles that were designed to operate on leaded fuel

^A Unleaded fuel having an antiknock index of at least 87 should also have a minimum Motor octane number of 82 in order to adequately protect those vehicles that are sensitive to Motor octane quality.

^B Reductions in vehicle antiknock requirements for altitude are shown in Fig. X1.2.

^C Reductions in vehicle antiknock requirements for seasonal variations are shown in Fig. X1.3.

^D Not all antiknock index levels listed in this table are available at all locations.

^E The Federal Trade Commission requires octane posting and certification in accordance with 16 CFR Part 308.

knock, that is, be "satisfied" with the octane quality of fuels at or above that level of antiknock index. The data in Fig. X1.1 are for new model cars and trucks sold in the United States in the model year 1988 and are included as an example of the antiknock requirement distribution, not as a data reference.

X1.4.7 According to the winter 1988-1989 motor gasoline survey published by the National Institute for Petroleum and Energy Research, unleaded fuel antiknock indexes in current practice range from a low near 84 in the mountain areas to a high of near 94. Companies typically market two or three unleaded grades of fuel, one of which usually has a minimum antiknock index of 87, for which most post-1971 vehicles are designed. Most companies also market a higher octane fuel with an antiknock index of 91 or above. This fuel is intended to satisfy those vehicles with a higher octane requirement. Some companies offer three grades of unleaded fuel. The third grade usually has an antiknock index of 89. Leaded fuel is still available in some markets and usually has an antiknock index of 88 or 89.

X1.4.8 Marketers set the grades and octane based on their perception of the technical and competitive needs in the market.

X1.4.9 Antiknock indexes of fuel sold in current practice in the United States are shown in Table X1.1 for both unleaded and leaded fuels.

X1.5 Precision and Bias of Antiknock Index

X1.5.1 The following statements apply to the precision and bias of antiknock index of fuel, which is a composite quantity not addressed in any other standard.

X1.5.2 The precision of the antiknock index, (RON + MON)/2, is a function of the individual precisions of Research (Test Method D 2699) and Motor (Test Method D 2700) octane numbers. The repeatability and reproducibility variances for these test methods are summed and divided by four to obtain the variance of the antiknock index.

X1.5.2.1 *Repeatability*—The difference between two sets of antiknock index determinations, where two test results by each octane number method were obtained by one operator, with the same apparatus under constant operating conditions on identical test material would, in the long run, and in the normal and correct operation of the test methods, exceed the values in the following table in only one case in twenty.

X1.5.2.2 *Reproducibility*—The difference between two independent sets of antiknock index determinations, obtained by different operators working in different laboratories on identical test material would, in the long run, and in the normal and correct operation of the test methods, exceed the values in the following table in only one case in twenty.

Antiknock Index	Repeatability, Antiknock Index Units	Reproducibility, Antiknock Index Units
83	0.2	0.7
85	0.2	0.7
87	0.2	0.6
89	0.2	0.6
91	0.2	0.6
93	0.2	0.6
95	—	0.6
97	—	0.7

NOTE X1.1—These precision values were calculated from Research and Motor octane number results utilizing exchange sample test data obtained by the ASTM National Exchange Group (NEG), the Institute of Petroleum, or the Institut Français du Pétrole, or combination thereof, participating in cooperative testing programs. The precision values for 83, 85, 95, and 97 AKI were obtained from NEG data during the period 1980 through 1982 and have been analyzed in accordance with RR: D02-1007, "Manual on Determining Precision Data for ASTM Methods on Petroleum Products and Lubricants," Spring 1973.¹⁰ The precision values for 87 through 93 AKI were calculated using the data from RR: D02-1383, "Research and Motor Octane Number Precision Study Report, 1988 through 1994," December 1995.¹¹

X1.5.2.3 *Bias*—Since knock ratings are determined by the conditions of the empirical test methods involved, bias cannot be determined.

X1.6 Effects of Altitude and Weather on Vehicle Antiknock Requirement

X1.6.1 A vehicle's antiknock requirement can vary with changes in altitude, ambient temperature, and humidity, depending on the control system of the vehicle. New vehicles have sensors to measure and engine management computers, which take into account such conditions as air charge temperature and barometric pressure. These vehicles are designed to have the same antiknock requirement at all altitudes and a reduced sensitivity to changes in ambient temperature. This more sophisticated control technology began to be used extensively in 1984. This technology, while constantly evolving and improving, is used on almost all new vehicles. This means that many vehicles in today's fleet require fuel having the same antiknock index regardless of changes in altitude or ambient temperatures. Older vehicles, which do not have sophisticated control systems, will likely experience changes in antiknock

¹⁰ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: D02-1007.

¹¹ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: D02-1383.

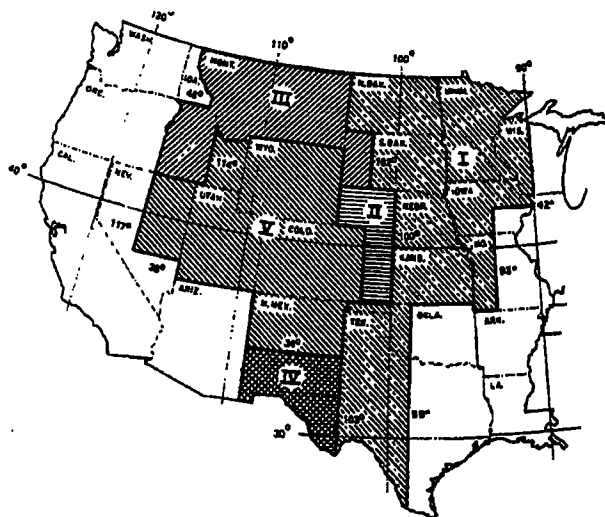


FIG. X1.2 Reduction in Vehicle Antiknock Requirements for Altitude^{A,B}

Area	Less than 89 AKI	89 AKI or Greater ^{A,B}
I	0.7	0.5
II	1.5	1.5
III	2.2	1.5
IV	3.0	2.0
V	4.5	3.0

^A Fuel may be marketed using these reductions, but actual antiknock index minimums must be posted.

^B While the reductions in this table apply to most pre-1984 vehicles, the control technology on almost all new vehicles will cause them to have no reduction in antiknock requirement at higher altitudes.

requirement due to changes in altitude and weather conditions. However, the changes in antiknock requirement indicated in the following sections apply to a continually smaller part of the vehicle fleet.

X1.6.2 The antiknock requirement of an older vehicle decreases as altitude increases, primarily due to reduction in mixture density caused by reduced atmospheric pressure. The change in antiknock requirement for altitude for older vehicles is given in Fig. X1.2. Boundaries of the areas defined and the corresponding antiknock index reductions were established to protect vehicles driven from a higher altitude to a lower altitude (and, hence higher antiknock requirement) area while using a fuel obtained in the high altitude area.

X1.6.3 Tests by CRC and other organizations have shown that the decrease in antiknock requirements with altitude is larger for most models between 1971 and 1984, designed to use a fuel with an antiknock index of 87, than for pre-1971 vehicles. Generally the pre-1971 vehicles have high compression ratios and were designed for fuels with an antiknock index of 88 or higher. Fuels with antiknock indexes below 89 are adjusted by a larger factor than those with an antiknock index of 89 or greater.

X1.6.4 The antiknock requirements of older vehicles rise with increasing ambient temperature on the average by 0.097 MON per degree Celsius (0.054 MON per degree Fahrenheit).

X1.6.5 The antiknock requirements of both older and new vehicles decrease with increasing specific humidity by 0.245

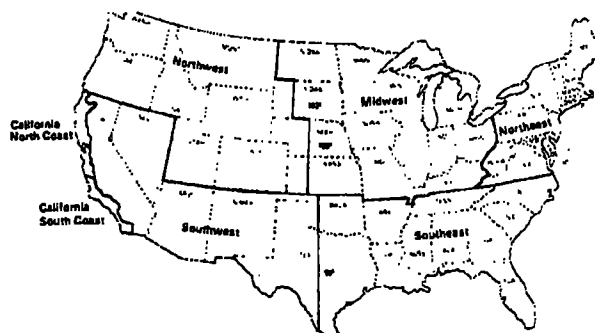


FIG. X1.3 Reduction in Vehicle Antiknock Requirements for Weather^A

	J	F	M	A	M	J	J	A	S	O	N	D
Northeast	1.0	0.5	0.5	0	0	0	0	0	0	0.5	0.5	1.0
Southeast	0.5	0	0	0	0	0.5	0.5	0.5	0.5	0	0	0.5
Midwest	1.0	0.5	0.5	0	0	0	0	0	0	0	0.5	1.0
Northwest	1.0	1.0	0.5	0.5	0	0	0	0	0	0.5	1.0	1.0
Southwest	1.0	0.5	0	0	0	0	0	0	0	0	0.5	1.0
California ^{A,B}												
No Coast	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0	0	0.5	0.5
So Coast	0	0	0.5	0.5	1.0	1.0	1.0	0.5	0.5	0	0	0
Alaska	1.0	1.0	0.5	0.5	0	0	0	0	0	0.5	1.0	1.0
Hawaii	0	0	0	0	0	0	0	0	0	0	0	0

^A Fuel may be marketed using these reductions, but actual antiknock index minimums must be posted.

^B Details of California coastal areas are shown in Footnote G of Table 4.

MON per gram of water per kilogram of dry air (0.035 MON per grain of water per pound of dry air).

X1.6.6 Because temperature and humidity of geographical areas are predictable throughout the year from past weather records, antiknock index levels can be adjusted to match seasonal changes in vehicle antiknock requirements. Fig. X1.3 defines the boundaries of areas and the typical reduction in vehicle antiknock requirements for weather for older vehicles. This figure may not apply to newer vehicles.

X1.7 Leaded Versus Unleaded Fuel Needs

X1.7.1 In addition to selecting the appropriate antiknock index to meet vehicle antiknock needs, a choice must be made between leaded and unleaded fuel. Vehicles that must use unleaded fuel are required by Environmental Protection Agency regulation to have permanent labels on the instrument panel and adjacent to the fuel tank filler inlet reading "Unleaded Fuel Only." Most 1975 and later model passenger cars and light trucks are in this category. Most 1971-1974 vehicles can use leaded or unleaded fuel. Pre-1971 vehicles were designed for leaded fuel; however, unleaded fuel of suitable antiknock index may generally be used in these vehicles, except that leaded fuel should be used periodically (after a few tankfuls of unleaded fuel have been used). Leaded fuel may be required in some vehicles, particularly trucks, in heavy-duty service and some farm equipment. Instructions on fuel selection are normally provided in publications of vehicles manufacturers (for example, owner's manuals, service bulletins, and so forth). Antiknock agents other than lead alkyls may be used to increase the antiknock index of fuels, and their concentrations may also be limited due to either performance or legal requirements.

X1.8 Volatility

X1.8.1 In most spark-ignition internal combustion engines, the fuel is metered in liquid form through the carburetor or fuel injector, and is mixed with air and partially vaporized before entering the cylinders of the engine. Consequently, volatility is an extremely important characteristic of motor fuel.

X1.8.2 At high operating temperatures, fuels can boil in fuel pumps, lines, or carburetors. If too much vapor is formed, the fuel flow to the engine can be decreased, resulting in loss of power, rough engine operation, or engine stoppage. These conditions are known as "vapor lock." Conversely, fuels that do not vaporize sufficiently can cause hard starting of cold engines and poor warm-up performance. These conditions can be minimized by proper selection of volatility requirements, but cannot always be avoided. For example, during spring and fall, a fuel of volatility suitable for satisfactory starting at low ambient temperatures can cause problems in some engines under higher ambient temperature operating conditions.

X1.8.3 Six vapor pressure/distillation classes and six vapor lock protection (vapor-liquid ratio) classes of fuel are provided to satisfy vehicle performance requirements under different climatic conditions and to comply with U.S. EPA vapor pressure limits for the control period of May 1 through September 15. Class A and Class AA specify the EPA maximum vapor pressure limits of 9.0 psi and 7.8 psi, respectively. Volatility of fuel is specified by an alphanumeric designation. The letter specifies the vapor pressure/distillation class and the number specifies the vapor lock protection class. The vapor pressure/distillation classes are needed to comply with the EPA vapor pressure regulations and are not based on vehicle performance during the EPA control period. The separate vapor lock protection classes are provided because under most ambient conditions, the EPA regulations specify a lower vapor pressure than would be required to prevent hot fuel handling problems. If the corresponding and unnecessarily more restrictive vapor-liquid ratios were specified when the EPA regulations are in effect, it could result in reduced fuel production, manufacturing hardships, and increased fuel costs. The schedule for seasonal and geographical distribution indicates the appropriate alphanumeric volatility requirement or requirements for each month in all areas of the United States, based on altitude and expected air temperatures, and on EPA vapor pressure regulations. Volatility limits are established in terms of vapor-liquid ratio, vapor pressure, and distillation properties.

X1.8.4 For sea-level areas outside of the United States where vapor pressure requirements are not as restrictive as those specified by EPA, the following ambient temperatures are for guidance in selecting the appropriate alphanumeric designation:

Alphanumeric Volatility Designation	10th Percentile 6-h Minimum Daily Temperature, °C (°F)	90th Percentile Maximum Daily Temperature, °C (°F)
A-1	>16 (60)	≥43 (110)
B-2	>10 (50)	<43 (110)
C-3	>4 (40)	<36 (97)
D-4	>-7 (20)	<29 (85)
E-5	≤-7 (20)	<21 (69)

The 6-h minimum temperature is the highest temperature of the six coldest consecutive hourly temperature readings of a 24-h day. The 6-h minimum temperature provides information on the cold-soak temperature experienced by a vehicle. The 10th percentile of this temperature statistic indicates a 10 % expectation that the 6-h minimum temperature will be below this value during a month. The 90th percentile maximum temperature is the highest temperature expected during 90 % of the days, and provides information relative to peak vehicle operating temperatures during warm and hot weather. For areas above sea level, the 10th percentile 6-h minimum temperature should be increased by 3.6°C/1000 m (2°F/1000 ft) of altitude, and the 90th percentile maximum should be increased by 4.4°C/1000 m (2.4°F/1000 ft) of altitude before comparing them to the sea level temperature. These corrections compensate for changes in fuel volatility caused by changes in barometric pressure due to altitude.

X1.9 Vapor Pressure

X1.9.1 The vapor pressure of fuel must be sufficiently high to ensure ease of engine starting, but it must not be so high as to contribute to vapor lock or excessive evaporative emissions and running losses.

X1.9.2 Test Methods D 4953, D 5190, D 5191, or D 5482 provide procedures for determining the vapor pressures of gasoline or gasoline-oxygenate blends.

X1.10 Vapor-Liquid Ratio

X1.10.1 Vapor-liquid ratio (V/L) is the ratio of the volume of vapor formed at atmospheric pressure to the volume of fuel tested in Test Method D 2533. The V/L increases with temperature for a given fuel. Because some oxygenates are miscible with the glycerin confining fluid, Test Method D 2533 has been modified so mercury can also be used as a confining fluid. Either procedure may be used for determining V/L of gasoline. The mercury confining fluid shall be used for gasoline-oxygenate blends. Test Method D 5188 is an evacuated chamber method for determining temperatures for vapor-liquid ratios between 8 to 1 and 75 to 1. Test Method D 5188 is applicable to both gasoline and gasoline-oxygenate blends.

X1.10.2 The temperature of the fuel system and the V/L that can be tolerated without vapor lock vary from vehicle to vehicle and with operating conditions. The tendency of a fuel to cause vapor lock, as evidenced by loss of power during full-throttle accelerations, is indicated by the gasoline temperature at a V/L of approximately 20. A similar relationship for gasoline-oxygenate blend has also been determined. The temperature at which the maximum V/L is specified for each gasoline volatility class is based on the ambient temperatures and the altitude associated with the use of the class.

X1.11 Vapor-Liquid Ratio (Estimated)

X1.11.1 Three techniques for estimating temperature- V/L values using vapor pressure (Test Methods D 4953, D 5190, D 5191, or D 5482) and distillation (Test Method D 86) results are given in Appendix X2; they apply to gasoline only.

X1.12 Distillation

X1.12.1 Test Method D 86 for distillation provides another measure of the volatility of fuels. Table 1 designates the limits for endpoint temperature and the temperatures at which 10 %, 50 %, and 90 % by volume of the fuel is evaporated. These distillation characteristics, along with vapor pressure and *V/L* characteristics, affect the following vehicle performance characteristics: starting, driveability, vapor lock, dilution of the engine oil, fuel economy, and carburetor icing.

X1.12.2 The 10 % evaporated temperature of fuel should be low enough to ensure starting under normal temperatures.

X1.12.3 Fuels having the same 10 % and 90 % evaporated temperatures can vary considerably in driveability performance because of differences in the boiling temperatures of the intermediate components, or fractions. Driveability and idling quality are affected by the 50 % evaporated temperature. The 90 % evaporated and endpoint temperatures should be low enough to minimize dilution of the engine oil.

X1.12.4 The ASTM Driveability Task Force has determined from data collected by CRC and others that a relationship exists between fuel distillation temperatures and vehicle cold start and warm-up driveability performance. This relationship can be expressed by a Driveability Demerit model that can estimate vehicle driveability demerits during cold start and warm-up conditions. The predictive model is a function of ambient temperature and fuel volatility expressed as the distillation temperatures at which 10 %, 50 %, and 90 % by volume of the fuel is evaporated. The Driveability Index ($DI = 1.5 T_{10} + 3.0 T_{50} + 1.0 T_{90}$), as shown in Table 1, is a simplified and more easily applied form of the Driveability Demerit model. A more detailed explanation of the DI equation development can be found in SAE Paper 881668.¹²

X1.13 Corrosion

X1.13.1 Fuels must pass the copper strip corrosion test to minimize corrosion in fuel systems due to sulfur compounds in the fuel. Some fuels corrode fuel system metals other than copper, but there are no ASTM test methods to evaluate corrosion of these metals. Depending on the type and concentration of oxygenate, gasoline-oxygenate blends can corrode metals such as zinc, magnesium, aluminum, steel, and ternite. However, at this time there is no test method with a known correlation to field performance. Consequently, additional corrosion tests are needed.

X1.14 Solvent-Washed Gum Content

X1.14.1 The test for solvent-washed gum content measures the amount of residue after evaporation of the fuel and following a heptane wash. The heptane wash removes the heptane-soluble, non-volatile material such as additives, carrier oils used with additives, and heavier hydrocarbons such as diesel fuels, and so forth. Solvent-washed gum consists of fuel-insoluble gum and fuel-soluble gum. The fuel-insoluble

portion can clog fuel filters. Both can be deposited on surfaces when the fuel evaporates.

X1.14.2 Solvent-washed gum can contribute to deposits on the surfaces of carburetors, fuel injectors, and intake manifolds, ports, valves, and valve guides. The impact of solvent-washed gum on malfunctions of modern engines is not well established and the current specification limit is historic rather than the result of recent correlative studies. It depends on where the deposits form; the presence of other deposit precursors, such as airborne debris, blowby and exhaust gas recirculation gases, and oxidized engine oil; and the amount of deposits.

X1.14.3 The difference between the unwashed and solvent-washed gum content values can be used to assess the presence and amount of nonvolatile material in the fuel. Additional analytical testing is required to determine if the material is additive, carrier oil, diesel fuel, and so forth.

X1.15 Sulfur

X1.15.1 The limit on sulfur content is included to protect against engine wear, deterioration of engine oil, and corrosion of exhaust system parts.

X1.16 Oxidation Stability

X1.16.1 The induction period as measured in the oxidation stability test is used as an indication of the resistance of fuel to gum formation in storage. Experience indicates that fuels with an induction period equal to or greater than that in Table 2 generally have acceptable short-term storage stability. However, correlation of the induction period with the formation of gum in storage can vary markedly under different storage conditions and with different fuels.

X1.17 Water Tolerance

X1.17.1 Water tolerance is the ability of a fuel to dissolve water without phase separation. It is not of concern for gasoline because of the very low solubility of water in hydrocarbons. Water tolerance is of some concern with gasoline-ether blends because of the limited solubility of ethers in water, but it is of great concern for gasoline-alcohol blends because of the very high solubility of alcohols in water. As such, Test Method D 6422 has been developed to determine the water tolerance (phase separation) characteristics of gasoline-alcohol blends. If the amount of water exceeds the water tolerance limit of the blend, the fuel will separate into a lower, alcohol-rich aqueous phase and an upper, alcohol-lean hydrocarbon phase. The resultant aqueous phase is not suitable as an automotive fuel and may be corrosive to many metals. Similarly, the hydrocarbon portion may also not be suitable as a fuel since removal of the alcohol component will change the volatility and antiknock characteristics.

X1.17.2 The most important factor, besides the quantity of water contacted, which governs the water tolerance of a fuel, is its temperature. As the temperature of the blend decreases, water tolerance decreases. Test Method D 6422 is intended to determine the ability of gasoline-alcohol blends to retain water in solution or in a stable suspension at the lowest temperature to which they are likely to be exposed in use. Some other

¹² Barker, D. A., Gibbs, L. M., and Steinke, E. D., "The Development and Implementation of the ASTM Driveability Index," SAE Paper 881668, 1988. Available from Society of Automotive Engineers, 400 Commonwealth Drive, Warrendale, PA 15096.

factors that affect water tolerance are alcohol concentration and aromatics content of the fuel.

X1.17.3 With some gasoline-oxygenate blends, formation of a haze may occur when filling a storage tank that contains water bottoms, while commingling of gasoline-oxygenate blends with gasoline, or when a sufficient decrease in temperature occurs. However, the haze may not be stable and the fuel will clear usually in a short period of time.

X1.17.4 A more critical water tolerance concern is the potential increase in storage tank water bottoms. This can occur when some gasoline-oxygenate blends and gasoline-alcohol blends in particular are added to a tank that contains sufficient water to extract some or all of the oxygenate component from the fuel.

X2. ESTIMATING TEMPERATURE-V/L VALUES FOR GASOLINE

X2.1 Scope

X2.1.1 Three techniques are presented here for estimating temperature-V/L data from vapor pressure and distillation test results¹³ on gasolines only. They are provided for use as a guideline when V/L data measured by Test Method D 2533 are not available. One method is designed for computer processing, one is a simpler linear technique, while the other is a nomogram form of this linear equation.

X2.1.2 These techniques are not optional procedures for measuring V/L. They are supplementary tools for estimating temperature-V/L relationships with reasonable accuracy when used with due regard for their limitations.

X2.1.3 Test Method D 2533 is the referee V/L procedure and shall be used when calculated values are questionable.

X2.1.4 These techniques are not intended for, nor are they necessarily applicable to, fuels of extreme distillation or chemical characteristics, such as would be outside the range of normal commercial motor gasolines. Thus, they are not applicable in all instances to gasoline blending stocks or specially blended fuels.

X2.2 Computer Method

X2.2.1 *Summary*—The values of four intermediate functions, A , B , C , and D , are derived from the gasoline vapor pressure and distillation temperatures at 10, 20, and 50 % evaporated. Values for A , B , C , and D can be obtained either from equations or from a set of charts. Sections X2.2.2.1-X2.2.2.3 provide A , B , C , and D values using SI units; X2.2.2.6-X2.2.2.8 provide A , B , C , and D values using inch-pound units. Estimated temperatures at a V/L of 4, 10, 20, 30, and 45 are then calculated from A , B , C , and D . Estimated temperatures at an intermediate V/L can be obtained by interpolation.

X2.2.2 Procedure:

X2.2.2.1 Establish input data from vapor pressure (Test Methods D 4953, D 5190, D 5191, or D 5482) and distillation (Test Method D 86) test results as follows:

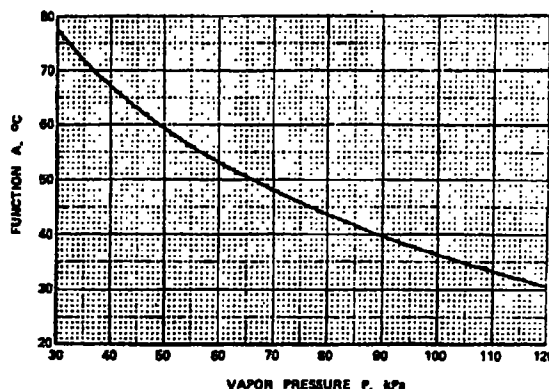


FIG. X2.1 Function A versus Vapor Pressure P

E = distillation temperature, °C at 10 % evaporated,

F = distillation temperature, °C at 20 % evaporated,

G = distillation temperature, °C at 50 % evaporated,

$$H = G - E, \text{ } ^\circ\text{C}, \quad (\text{X2.1})$$

$$P = \text{vapor pressure, kPa},$$

$$Q = F - E, \text{ } ^\circ\text{C}, \text{ and} \quad (\text{X2.2})$$

$$R = H/Q, \text{ except that if } H/Q \text{ is greater than } 6.7, \text{ make } R = 6.7. \quad (\text{X2.3})$$

X2.2.2.2 If A , B , C , and D are to be calculated, use the following equations:

$$A = 102.859 - 1.36599P + 0.009617P^2 - 0.000028281P^3 + 207.0097/P \quad (\text{X2.4})$$

$$B = -5.36868 + 0.910540Q - 0.040187Q^2 + 0.00057774Q^3 + 0.254183/Q \quad (\text{X2.5})$$

$$S = -0.00525449 - 0.3671362/(P - 9.65) - 0.812419/(P - 9.65)^2 + 0.0009677R - 0.0000195828R^2 - 3.3502318R/P^2 + 1241.1531R/P^4 - 0.06630129R^2/P + 0.00627839R^3/P + 0.0969193R^2/P^2 \quad (\text{X2.6})$$

$$C = 0.34205P + 0.55556/S \quad (\text{X2.7})$$

$$D = 0.62478 - 0.68964R + 0.132708R^2 - 0.0070417R^3 + 5.8485/R \quad (\text{X2.8})$$

X2.2.2.3 If A , B , C , and D are to be obtained from charts, read them from Figs. X2.1-X2.4, respectively.

X2.2.2.4 Calculate the estimated temperature (°C or °F) at V/L ratios 4, 10, 20, 30, and 45 from the following equations:

$$T_4 = A + B \quad (\text{X2.9})$$

¹³ A correlation of temperature-V/L ratio data with vapor pressure and distillation data was developed in 1943 and restudied in 1963 by panels of the Coordinating Research Council, Inc. See "Correlation of Gasoline Vapor Forming Characteristics with Inspection Test Data," *CRC Report No. 159*, Jan. 28, 1943 (or SAE Transaction, Vol 52, August 1944, pp. 364-367) and "Study of CRC Calculated Temperature-V/L Technique," *CRC Report No. 370*, February 1963. The CRC correlation was modified by a task group of Subcommittee A of Committee D02 to adapt it for computer processing, as well as the linear equation and the nomogram.

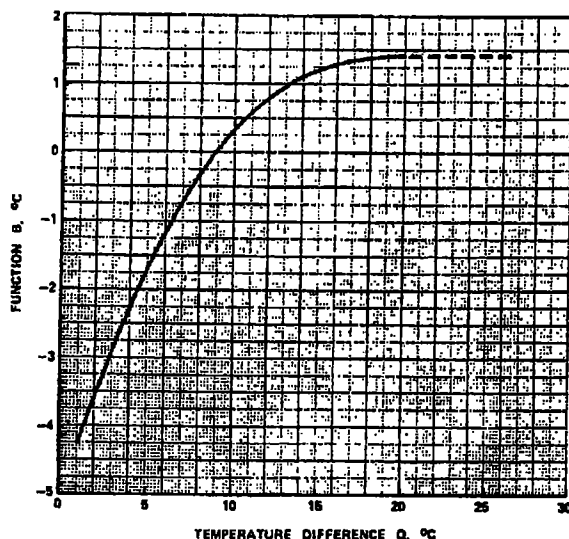


FIG. X2.2 Function B versus Distillation Temperature Difference Q

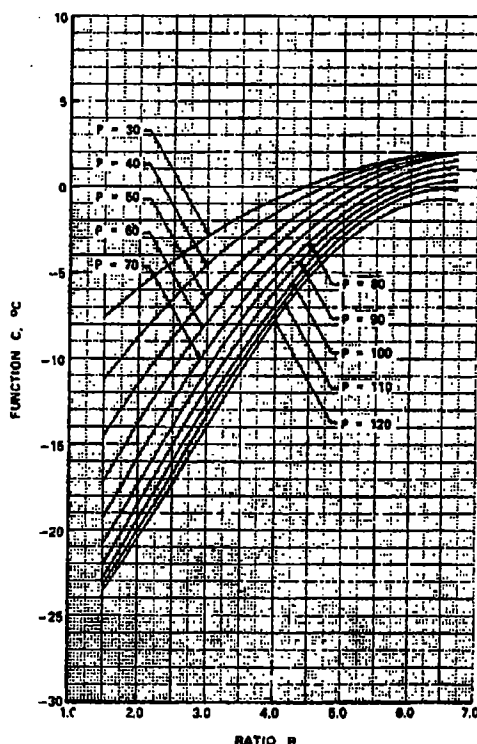


FIG. X2.3 Function C versus Ratio R and Vapor Pressure P

$$T45 = F + 0.125H + C \quad (X2.10)$$

$$T10 = T4 + 0.146341(T45 - T4) + D \quad (X2.11)$$

$$T20 = T4 + 0.390244(T45 - T4) + 1.46519D \quad (X2.12)$$

$$T30 = T4 + 0.634146(T45 - T4) + D \quad (X2.13)$$

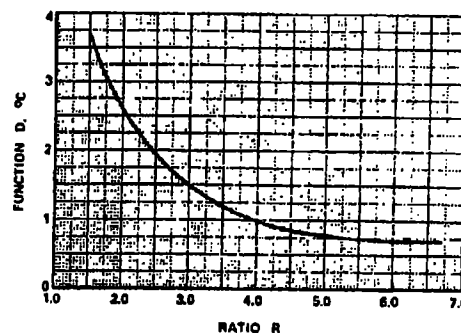


FIG. X2.4 Function D versus Ratio R

where:

T4, T10, T20, T30, and T45 are estimated temperatures at V/L ratios, 4, 10, 20, 30, and 45, respectively.

X2.2.2.5 If the temperature at an intermediate V/L ratio is to be estimated, either plot the values calculated in X2.2.2.4 and read the desired value from a smooth curve through the points, or use the Lagrange interpolation formula as follows:

$$\begin{aligned} TX = & T4 \left(\frac{X-10}{4-10} \times \frac{X-30}{4-30} \times \frac{X-45}{4-45} \right) \\ & + T10 \left(\frac{X-4}{10-4} \times \frac{X-30}{10-30} \times \frac{X-45}{10-45} \right) \\ & + T30 \left(\frac{X-4}{30-4} \times \frac{X-10}{30-10} \times \frac{X-45}{30-45} \right) \\ & + T45 \left(\frac{X-4}{45-4} \times \frac{X-10}{45-10} \times \frac{X-30}{45-30} \right) \end{aligned} \quad (X2.14)$$

where:

X = the desired V/L ratio between 4 and 45, and

TX = the estimated temperature at V/L ratio X.

X2.2.2.6 If inch-pound units are used, establish input data from vapor pressure (Test Methods D 4953, D 5190, D 5191, or D 5482) and distillation (Test Method D 86) test results as follows:

E = distillation temperature, °F at 10 % evaporated,

F = distillation temperature, °F at 20 % evaporated,

G = distillation temperature, °F at 50 % evaporated,

$$H = G - E, \text{ °F} \quad (X2.15)$$

P = vapor pressure, psi,

$$Q = F - E, \text{ °F, and} \quad (X2.16)$$

$$R = H/Q, \text{ except that if } H/Q \text{ is greater than 6.7, make } R = 6.7. \quad (X2.17)$$

X2.2.2.7 If A, B, C, and D are to be calculated in inch-pound units, use the following equations:

$$A = 217.147 - 16.9527P + 0.822909P^2 - 0.0166849P^3 + 54.0436/P \quad (X2.18)$$

$$B = -9.66363 + 0.910540Q - 0.0223260Q^2 + 0.000178314Q^3 + 0.823553/Q \quad (X2.19)$$

$$S = -0.00525449 - 0.0532486/(P - 1.4) - 0.0170900/(P - 1.4)^2 + 0.0009677R -$$

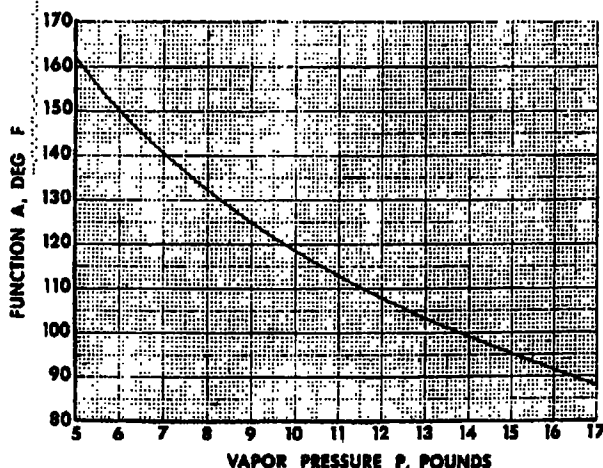


FIG. X2.5 Function A versus Vapor Pressure P

$$0.0000195828R^2 - 0.0704753R/P^2 + 0.549224R/P^4 - 0.00961619R^2/P + 0.000910603R^3/P + 0.00203879R^2/P^2 \quad (X2.20)$$

$$C = 4.245P + 1.0/S \quad (X2.21)$$

$$D = 1.12460 - 1.24135R + 0.238875R^2 - 0.0126750R^3 + 10.5273/R \quad (X2.22)$$

X2.2.2.8 If A, B, C, and D are to be obtained from charts in inch-pound units, read them from Figs. X2.5-X2.8, respectively.

X2.2.2.9 Calculate the estimated temperatures, °F, at V/L ratios 4, 10, 20, 30, and 45 using the equations in X2.2.2.4 and X2.2.2.5.

X2.3 Linear Equation Method

X2.3.1 *Summary*—As given, these two equations provide only the temperatures (°C or °F) at which a V/L value of 20 exists. They make use of two points from the distillation curve, T_{10} (°C or °F), and the vapor pressure (kPa or psi) of the gasoline with constant weighting factors being applied to each. Experience has shown that data obtained with these simple linear equations generally are in close agreement with those obtained by the computerized version given above. The limitations pointed out in X2.1.1-X2.1.4 must be kept in mind when use is made of this procedure.

X2.3.2 *Procedure*—Obtain 10 % evaporated and 50 % evaporated points from the distillation curve (Test Method D 86) along with the vapor pressure value (Test Methods D 4953, D 5190, D 5191, or D 5482); apply these directly in the equation.

$$T_{V/L=20} = 52.47 - 0.33 (VP) + 0.20 T_{10} + 0.17 T_{50} \quad (X2.23)$$

where:

$T_{V/L=20}$ = temperature, °C, at V/L of 20:1,
 VP = vapor pressure, kPa,
 T_{10} = distillation temperature, °C, at 10 % evaporated, and
 T_{50} = distillation temperature, °C, at 50 % evaporated.

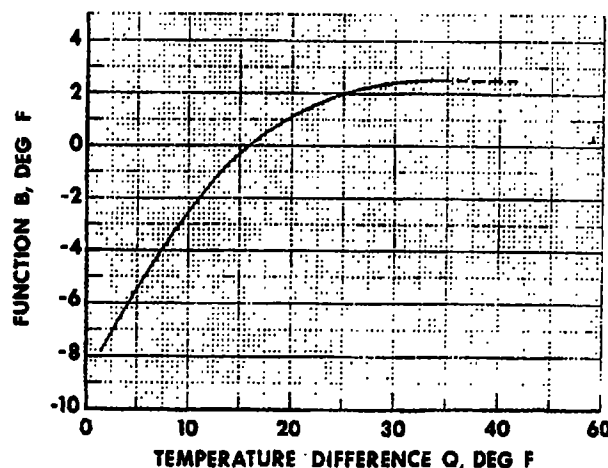


FIG. X2.6 Function B versus Distillation Temperature Difference Q

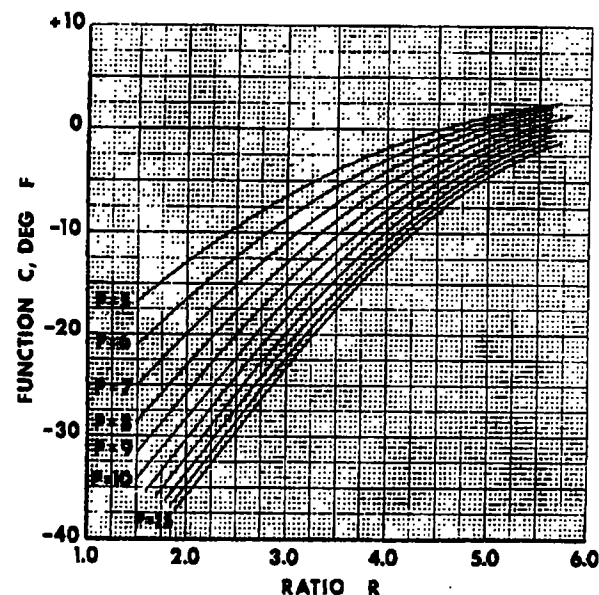


FIG. X2.7 Function C versus Ratio R and Vapor Pressure P

or in the inch-pound customary unit equation:

$$T_{V/L=20} = 114.6 - 4.1 (VP) + 0.20 T_{10} + 0.17 T_{50} \quad (X2.24)$$

where:

$T_{V/L=20}$ = temperature, °F, at V/L of 20:1,
 VP = vapor pressure, psi,
 T_{10} = distillation temperature, °F, at 10 % evaporated, and
 T_{50} = distillation temperature, °F, at 50 % evaporated.

X2.4 Nomogram Method

X2.4.1 *Summary*—Two nomograms have been developed and are included in this specification (Figs. X2.9 and X2.10) to provide the same function as the linear equations procedure

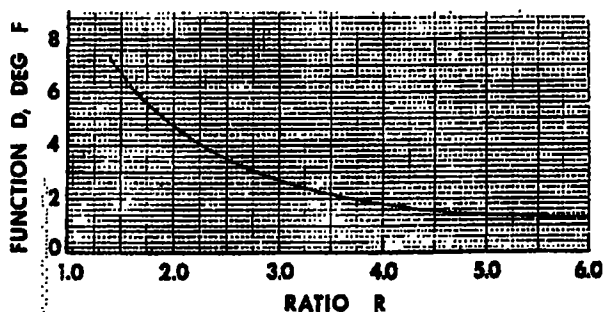


FIG. X2.8 Function D versus Ratio R

outlined above. Fig. X2.9 is in SI units and Fig. X2.10 is in inch-pound units. The nomograms are based on the two equations and the same limitations apply to their use in estimating V/L (20) temperatures.

X2.4.2 Procedure—Obtain 10 % evaporated and 50 % evaporated points from the distillation curve (Test Method D 86) along with the vapor pressure value (Test Methods D 4953, D 5190, D 5191, or D 5482). Select the SI unit (Fig. X2.9) or inch-pound unit (Fig. X2.10) nomogram based on the units of T_{10} , T_{50} , and VP. Using a straightedge, locate the intercept on the line between the " T_{10} and T_{50} " scales after selecting the applicable T_{10} and T_{50} values. From this intercept and the proper point on the "VP" scale, a second intercept can be obtained on the " $T_{V/L=20}$ " scale to provide the desired value directly.

X2.5 Precision

X2.5.1 The precision of agreement between temperature- V/L data estimated by any one of these three techniques and data obtained by Test Method D 2533 has not been established.

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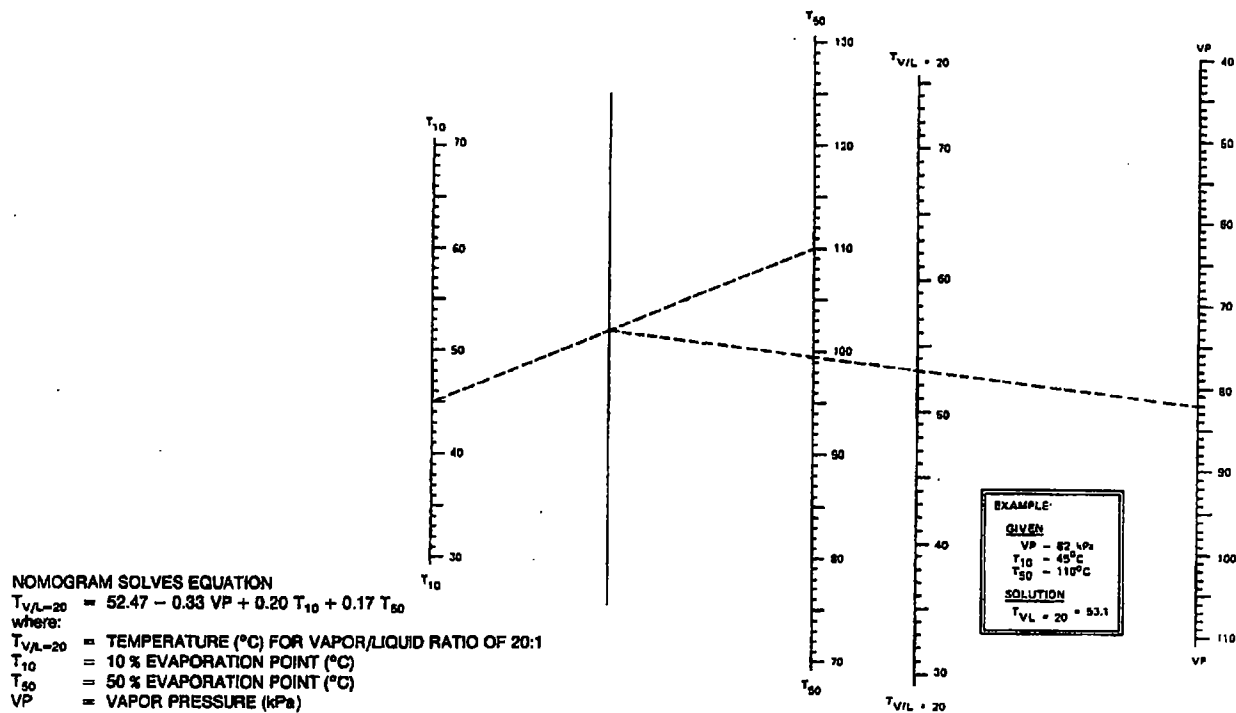


FIG. X2.9 Relationship Between Gasoline Volatility and Temperature for V/L Ratio at Sea Level—SI Units

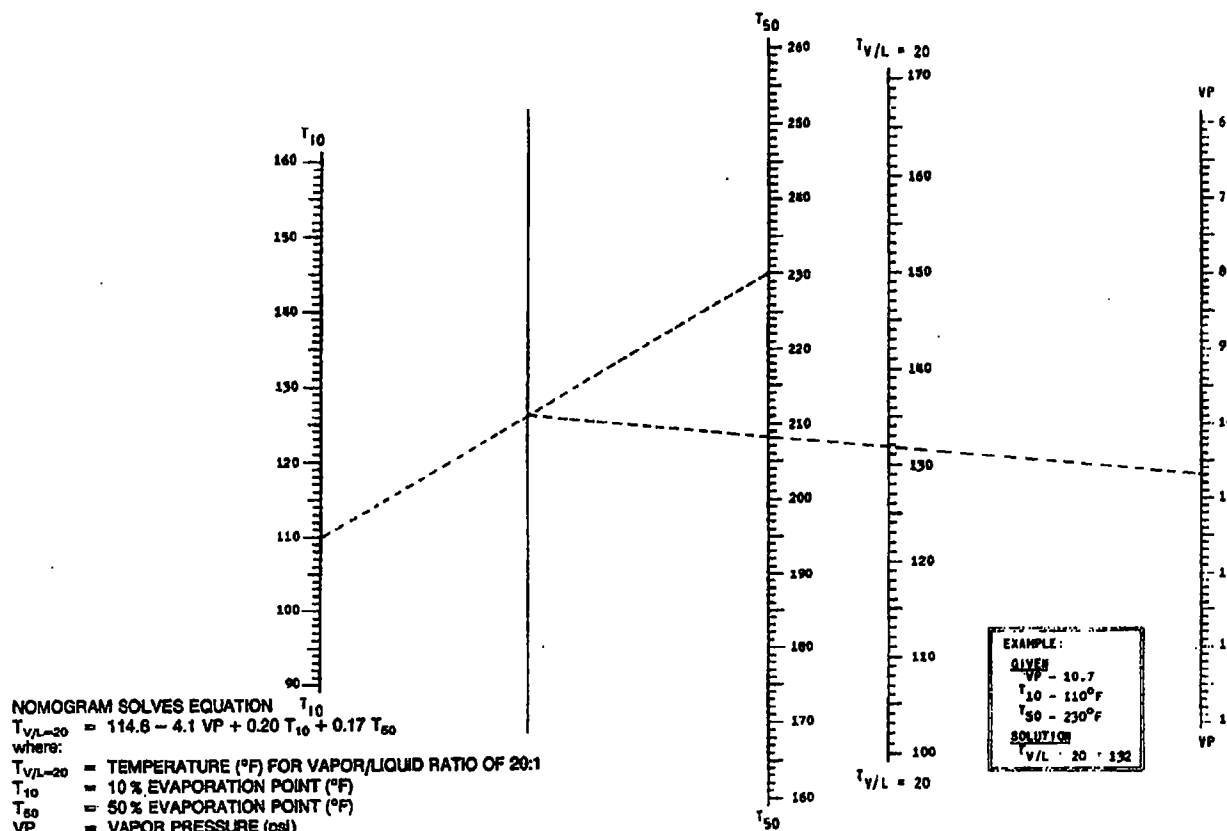


FIG. X2.10 Relationship Between Gasoline Volatility and Temperature for V/L Ratio of 20 at Sea Level—Inch-Pound Units

X3. SUMMARY OF EPA REGULATIONS APPLICABLE TO SPARK-IGNITION ENGINE FUEL

X3.1 EPA Applicable Vapor Pressure Standards

X3.1.1 Under authority of the Clean Air Act, the U.S. Environmental Protection Agency (EPA) issued, effective May 1992, vapor pressure control standards for leaded and unleaded gasoline and leaded and unleaded gasoline-oxygenate blends. Some states, notably California, have more restrictive vapor pressure limits.

X3.1.2 Details of the EPA regulations and test methods are available in Part 80 of Title 40 of the Code of Federal Regulations (40 CFR Part 80). For specific state vapor pressure regulations, the state of interest should be contacted.

X3.1.3 The EPA maximum vapor pressure limits of 7.8 psi and 9.0 psi are shown in Table 1 as Classes AA and A, respectively. The EPA requirements for each distribution area are shown in Table 4 for the period May 1 through September 15. For the month of May, the EPA limits only apply to finished gasoline and gasoline-oxygenate blend tankage at refineries, importers, pipelines, and terminals. For the period June 1 through September 15, the EPA limits apply to all locations of the distribution system. Footnotes D through F of Table 4 indicate the ozone nonattainment areas which are limited to 7.8 psi maximum and the appropriate vapor lock protection class.

California has controls that vary for the different air basins from as early as March 1 at refineries through as late as October 31. There are no EPA vapor pressure limits for the states of Alaska or Hawaii.

X3.1.4 EPA regulations allow 1.0 psi higher values for gasoline-ethanol blends than the EPA limits shown in Table 1 and Table 4 for the period May 1 through September 15. To qualify, the gasoline-ethanol blends must contain 9 to 10 volume % ethanol. Higher vapor pressure limits for gasoline-ethanol blends under state regulations vary for other time periods, and specific states of interest should be contacted to determine if higher limits apply.

X3.2 EPA Lead and Phosphorus Regulations

X3.2.1 *Unleaded Fuel*—The intentional addition of lead or phosphorus compounds to unleaded fuel is not permitted by the EPA. EPA regulations limit their maximum concentrations to 0.05 g lead/U.S. gal (0.013 g/L) and 0.005 g of phosphorus/U.S. gal (0.0013 g/L) (see Test Method D 3231), respectively.

X3.2.2 *Leaded Fuel*—EPA regulations after December 31, 1995 prohibit the sale, supply, dispensing, transporting, or introducing into commerce a fuel for use in any motor vehicle

which is produced with the use of lead additives or which contains more than 0.05 g lead/U.S. gal (0.013 g/L).

X3.2.2.1 The regulations define motor vehicle to include any self-propelled vehicle designed for transporting persons or property on a street or highway.

X3.2.2.2 The regulations do not prohibit the use of lead additives in fuel used in aircraft, racing cars, and nonroad engines, such as farm equipment engines and marine engines.

X3.3 EPA Oxygenate Regulations Applicable to Unleaded Gasoline-Oxygenate Blends

X3.3.1 Substantially Similar Rule:

X3.3.1.1 Section 211(f) (1) of the Clean Air Act prohibits introducing into commerce or increasing the concentration in use of, any fuel or fuel additive, which is not substantially similar to any fuel or fuel additive utilized for emissions certification of any model year 1975, or subsequent model year vehicle or engine, unless a waiver is obtained from the EPA.

X3.3.1.2 Gasoline-oxygenate blends are considered "substantially similar" if the following criteria are met.

(1) The fuel must contain carbon, hydrogen, and oxygen, nitrogen, or sulfur, or combination thereof, exclusively, in the form of some combination of the following:

- (a) Hydrocarbons;
- (b) Aliphatic ethers;
- (c) Aliphatic alcohols other than methanol;
- (d) (i) Up to 0.3 volume % methanol;

(ii) Up to 2.75 volume % methanol with an equal volume of butanol, or higher molecular weight alcohol;

(2) The fuel must contain no more than 2.0 mass % oxygen except fuels containing aliphatic ethers and/or alcohols (excluding methanol) must contain no more than 2.7 mass % oxygen.

(3) The fuel must possess, at the time of manufacture, all of the physical and chemical characteristics of an unleaded gasoline as specified by Specification D 4814 - 88 for at least one of the Seasonal and Geographical Volatility Classes specified in the standard.

NOTE X3.1—Opinion varies as to whether the EPA "substantially similar" rule requires unleaded gasolines that do not contain oxygenates to meet ASTM specifications.

X3.3.2 Waivers:

X3.3.2.1 EPA has issued waivers for blends of gasoline and ethanol (gasohol), gasoline and ethanol with cosolvents, and gasoline and methanol with cosolvents that are less limiting than the "substantially similar" rule. For the latest listing of waivers, EPA should be contacted.

X3.3.2.2 Gasoline-ethanol blends are not required by EPA to meet Specification D 4814 volatility limits (see X3.1.4 for vapor pressure limits). EPA has specified in all other waivers that the volatility of the finished gasoline-oxygenate blend must comply with Specification D 439 or D 4814 climatic and geographical limits.

X3.4 EPA Reformulated Gasoline (RFG)

X3.4.1 Reformulated gasoline (RFG) is a spark-ignition engine fuel formulated to reduce motor vehicle emissions of toxic and tropospheric ozone-forming compounds. The Clean

Air Act Amendments of 1990 require that RFG be sold in nine metropolitan areas with the worst summertime ozone levels. Other areas that do not meet ambient ozone standards may petition EPA to require RFG. The various RFG regulations have been established by the EPA. EPA has also placed limits on conventional gasoline sold in the rest of the U.S. to prevent RFG producers from using conventional gasoline as an outlet for undesirable fuel components (anti-dumping requirements). The EPA requirements became effective at the retail level on January 1, 1995.

X3.4.2 The characteristics of reformulated spark-ignition engine fuel, beyond those described by this specification, are described in the research report on reformulated spark-ignition engine fuel.² The research report also includes information on California Air Resources Board Phase 2 gasoline requirements, which are more restrictive than the EPA RFG requirements and take effect at the retail level on June 1, 1996.

X3.5 EPA Certification Standards for Deposit Control Gasoline Additives

X3.5.1 Beginning August 1, 1997, except for some fuel specific certifications, fuel sold or transferred to the ultimate consumer must contain detergent additive(s) meeting the EPA certification requirements. The regulation applies to fuels whether intended for on-highway or nonroad use, including conventional, reformulated, oxygenated, and leaded gasolines, as well as fuels used in marine service, and the gasoline component of M85 and E85 fuel alcohols. Racing fuel for non-highway use in racing vehicles and aviation fuel used in aircraft are exempted. Fuels used for research, development, and testing and federal emissions certification fuels can be exempted.

X3.5.2 As of July 1, 1997, only certified detergents may be used by detergent blenders, and distributors may only sell or transfer fuel that is properly additized with certified detergents. Detergent additives may be certified for nationwide use, for geographical use based on Petroleum Administration Districts for Defense (PADDs), or for a fuel-specific option for segregated gasoline pools. Certification sub-options allow a detergent to be certified for use in premium-grade, nonoxygenated, or oxygenate-specific fuel. A California Air Resources Board additive certification will be accepted for fuel additized or used only in California. Specific minimum fuel properties (aromatics, sulfur content, olefins content, and 90 % evaporated point) for each option are required for certification and the certification fuels must also meet the requirements of Specification D 4814-95c. For some options, the addition of 10 volume % ethanol is required for certification fuel. Other oxygenates may also be required. Testing is required to demonstrate that the certification fuels without additives form a minimum level of intake valve deposits if specially formulated from refinery blend stocks. Such deposit demonstration testing is not required for test fuels sampled directly from finished fuels, fuel-specific test fuels, CARB-based certifications, and leaded gasoline certifications.

X3.5.3 For additive certification, the test fuel containing the detergent additive(s) must form less than 100 mg/valve average intake valve deposit weight after 10 000 miles of testing in accordance with Test Method D 5500-94. In addition, after

10 000 miles of testing, there may be no more than 5 % flow restriction in any one fuel injector in accordance with Test Method D 5598-94.

X3.6 EPA Gasoline Sulfur Requirements (Tier 2)¹⁴

X3.6.1 Beginning in 2004, the basic EPA sulfur regulations require refiners to meet a corporate pool annual average sulfur maximum level of 120 parts per million (ppm), with a per gallon cap of 300 ppm. A provision in the rules allows a refinery to exceed the 300 ppm cap up to a maximum of 350 ppm for 2004. EPA has taken into account a 28 ppm test reproducibility which translates into a downstream enforcement standard of 378 ppm maximum (350+28). Anyone taking advantage of producing gasoline in excess of 300 ppm has to make up for the excess in their 2005 cap. For 2005, the corporate pool annual average decreases to 90 ppm maximum, the per gallon cap is at 300 ppm, and a refinery annual average maximum limit of 30 ppm is added. The downstream enforcement standard lowers to 326 ppm (300 ppm refinery cap plus 26 ppm test reproducibility). For 2006 and later, the refinery annual average remains at 30 ppm maximum, the per gallon cap is reduced to 80 ppm, and there no longer is a corporate pool annual average limit. The downstream enforcement standard is reduced to 95 ppm maximum (80 ppm refinery cap plus 15 ppm test reproducibility).

X3.6.2 Also beginning in 2004, there is a separate set of standards for a Geographical Phase-In Area Program (GPA)

¹⁴ Details of the sulfur regulations, including definitions, specific limits, effective dates, exceptions, and enforcement, are available in Parts 80.190 through 80.415 of Title 40 of the Code of Federal Regulations (40 CFR Parts 80.190-80.415).

which consists of the states of Alaska, Colorado, Idaho, Montana, New Mexico, North Dakota, Utah, and Wyoming, and selected regions of Arizona, Nebraska, Nevada, Oregon, South Dakota and Washington. The 2004 limits are the same as for the basic program, except there also is a 150 ppm maximum refinery annual average. For 2005, the refinery annual average remains at 150 ppm maximum while the corporate pool annual average and per gallon cap are the same as the basic program. If more than 50% of a refiner's gasoline is GPA in 2004 or 2005, the corporate pool average does not apply in 2004-2005. For 2006, the corporate pool annual average is eliminated while the other limits remain the same as for 2005. For 2007, the limits become the same as for the basic program with the refinery annual average at 30 ppm maximum and the per gallon cap at 80 ppm. The downstream enforcement level is at 95 ppm maximum (80 ppm refinery cap plus 15 ppm reproducibility tolerance). However, there is a process to obtain a two-year extension (through 2007 and 2008) of the 2006 limits where the GPA refinery agrees to also produce 15 ppm maximum sulfur diesel fuel beginning in 2006.

X3.6.3 For refiners that qualify for small refiner status, another set of sulfur limits applies for the period 2004 through 2007. The annual average sulfur level standard for each refinery is determined based on the refinery's 1997-1998 sulfur level baseline and the maximum ranges from 30 ppm to 300 ppm. The sulfur cap is similarly based and can range from 300 ppm to 450 ppm. Small refiners may also obtain a three-year extension (through 2008, 2009, and 2010) of the 2007 limits where the small refiner agrees to produce 15 ppm maximum sulfur diesel fuel beginning in 2006.

X4. METHOD FOR CALCULATING MASS PERCENT OXYGEN OF GASOLINE-OXYGENATE BLENDS

X4.1 Scope

X4.1.1 Test Method D 4815 provides a procedure for calculating the mass oxygen content of fuels using oxygenate concentration in mass percent. When oxygenate concentration in mass percent is not available, the oxygen concentration of these fuels can be determined indirectly by: (1) measuring the volume concentration of the oxygenates in the blend, which may be reported from Test Method D 4815 or equivalent method, (2) measuring the density or relative density of the blend, (3) converting the oxygenate concentrations from volume to mass concentrations, and (4) converting the mass oxygenate concentrations to mass oxygen concentrations using the oxygen mass fractions of the oxygenates present.

X4.2 Procedure

X4.2.1 The following steps are used to determine the total mass oxygen concentration of gasoline-oxygenate blends when indirect calculation is necessary.

X4.2.1.1 Determine the volume concentrations of oxygenates in a gasoline-oxygenate blend (Test Method D 4815 or equivalent test method).

X4.2.1.2 Determine the density or relative density of the gasoline-oxygenate blend (Test Methods D 287, D 1298, or D 4052).

X4.2.1.3 The oxygen mass percent of the gasoline-oxygenate blend is calculated using the following general equation. The densities or relative densities and oxygen mass fractions of a number of pure oxygenates are provided in Table X4.1 for use in Eq X4.1. The choice of density or relative density must be the same as determined in X4.2.1.2 for the gasoline-oxygenate blend.

$$\text{Oxygen, Mass \%} = \frac{V_1 \times d_1 \times O_1 + V_2 \times d_2 \times O_2 \dots + V_n \times d_n \times O_n}{V_b \times d_b} \times 100 \quad (\text{X4.1})$$

TABLE X4.1 Densities, Relative Densities, and Oxygen Mass Fractions of Pure Oxygenates

Oxygenate	Density, g/mL 20°C (68°F)	Relative Density 15.56/15.56°C (60/60°F)	Oxygen Mass Fraction
Methyl Alcohol	0.7913	0.7983	0.4993
Ethyl Alcohol	0.7894	0.7939	0.3473
n-Propyl Alcohol	0.8038	0.8080	0.2862
Isopropyl Alcohol	0.7855	0.7898	0.2862
n-Butyl Alcohol	0.8097	0.8137	0.2158
Isobutyl Alcohol	0.8016	0.8058	0.2158
sec-Butyl Alcohol	0.8069	0.8114	0.2158
tertiary-Butyl Alcohol	0.7886 ^A	0.7922 ^A	0.2158
Methyl tertiary-Butyl Ether	0.7406	0.7460	0.1815
Ethyl tertiary-Butyl Ether	0.7399	0.7452	0.1696
tertiary-Amyl Methyl Ether	0.7707	0.7758	0.1566
tertiary-Hexyl Methyl Ether	0.7815	0.7860	0.1377
Dilsopropyl Ether	0.7235	0.7282	0.1566

^A Extrapolated, below freezing temperature.

where:

- V_n = volume % of oxygenates 1 through n ,
- d_n = density or relative density of oxygenates 1 through n ,
- O_n = mass fraction oxygen in oxygenates 1 through n ,
- V_b = volume % of gasoline-oxygenate blend = 100, and
- d_b = density or relative density of gasoline-oxygenate blend.

X4.3 Example Calculation

X4.3.1 Assume that a gasoline-oxygenate blend is reported to contain 9.5 volume % ethanol and 2.0 volume % methyl tertiary-butyl ether and that the relative density of the blend is measured to be 0.7450, 15.56/15.56°C (60/60°F).

X4.3.2 Using the relative density and oxygen mass fraction data for ethanol and methyl tertiary-butyl ether from Table X4.1, the following mass % oxygen is calculated for this gasoline-oxygenate blend.

$$\text{Oxygen, Mass \%} = \frac{9.5 \times 0.7939 \times 0.3473 + 2.0 \times 0.7460 \times 0.1815}{100 \times 0.7450} \times 100 = 3.88 \quad (\text{X4.2})$$

X4.4 Precision

X4.4.1 The precision of this calculation method is a function of the individual precisions of density or relative density (Test Methods D 287, D 1298, or D 4052) and oxygenate analysis (Test Method D 4815 or equivalent). Because the repeatability and reproducibility vary with the analyses used, no estimate is provided.

X5. MICROBIAL CONTAMINATION

X5.1 Uncontrolled microbial contamination in fuel systems may cause or contribute to a variety of problems including increased corrosivity, and decreased stability, filterability, and caloric value. Microbial processes in fuel systems may also cause or contribute to system damage.

X5.2 Because the microbes contributing to the aforementioned problems may not be present in the fuel itself, no microbial quality criterion for fuels is recommended. However,

it is important that personnel responsible for fuel quality understand how uncontrolled microbial contamination may affect fuel quality.

X5.3 Guide D 6469 provides personnel with limited microbiological background an understanding of the symptoms, occurrences, and consequences of chronic microbial contamination. Guide D 6469 also suggests means for detecting and controlling microbial contamination in fuels and fuel systems.

X6. FUEL FILTRATION

X6.1 During the distribution of spark-ignition fuels, it is possible for them to become contaminated with potential filter blocking materials. While proper handling will minimize the

contamination levels, it is recommended that all fuel dispensers be equipped with filters of 10 µm or less nominal pore size at point of delivery to the customer.



D 4814 – 04a

SUMMARY OF CHANGES

Subcommittee D02.A0 has identified the location of selected changes to this standard since the last issue (D 4814–04) that may impact the use of this standard. (Approved July 1, 2004.)

- (1) Added new footnote to Table 2.
- (2) Added new X3.6.
- (3) Changed Table 6 for Colorado.

- (4) Changed sulfur limit for unleaded gasoline to comply with Federal Tier 2 sulfur regulations.

Subcommittee D02.A0 has identified the location of selected changes to this standard since the last issue (D 4814–03a) that may impact the use of this standard. (Approved June 1, 2004.)

- (1) Added Test Method D 5599 to 5.1 and the Referenced Documents.

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EXHIBIT B



Designation: D 4814 - 95c

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An American National Standard

Standard Specification for Automotive Spark-Ignition Engine Fuel¹

This standard is issued under the fixed designation D 4814; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

This standard has been approved for use by agencies of the Department of Defense. Consult the DoD Index of Specifications and Standards for the specific year of issue which has been adopted by the Department of Defense.

1. Scope

1.1 This specification guides in establishing requirements of automotive fuels for ground vehicles equipped with spark-ignition engines.

1.2 This specification describes various characteristics of automotive fuels for use over a wide range of operating conditions. It provides for a variation of the volatility and water tolerance of automotive fuel in accordance with seasonal climatic changes at the locality where the fuel is used. For the period May 1 through September 15, the maximum vapor pressure limits issued by the U.S. Environmental Protection Agency (EPA) are specified for each geographical area except Alaska and Hawaii. Variation of antiknock index with seasonal climatic changes and altitude is discussed in Appendix X1. This specification neither necessarily includes all types of fuels that are satisfactory for automotive vehicles, nor necessarily excludes fuels that can perform unsatisfactorily under certain operating conditions or in certain equipment. The significance of each of the properties of this specification is shown in Appendix X1.

1.3 The spark-ignition engine fuels covered in this specification are gasoline and its blends with oxygenates such as alcohols and ethers. This specification does not apply to fuels that contain an oxygenate as the primary component, such as Fuel Methanol (M85). The concentrations and types of oxygenates are not specifically limited in this specification. However, depending on oxygenate type, as oxygenate content increases above some threshold level, the likelihood for vehicle problems also increases. The composition of both unleaded and leaded fuel is limited by economic, legal, and technical consideration, but their properties, including volatility, are defined by this specification. In addition, the composition of unleaded fuel is subject to the rules, regulations, and Clean Air Act waivers of the U.S. Environmental Protection Agency (EPA). With regard to fuel properties, including volatility, this specification can be more or less restrictive than the EPA rules, regulations, and waivers. Refer to Appendix X3 for discussions of EPA rules relating to fuel volatility, lead and phosphorous contents, and use of oxygenates in blends with unleaded gasoline. Contact EPA for the latest versions of the rules and additional requirements.

1.4 This specification does not address the emission

characteristics of reformulated spark-ignition engine fuel. Reformulated spark-ignition engine fuel is required in some areas to lower emissions from automotive vehicles, and its characteristics are described in the research report on reformulated spark-ignition engine fuel.² However, in addition to the legal requirements found in this research report, reformulated spark-ignition engine fuel should meet the performance requirements found in this specification.

1.5 This specification represents a description of automotive fuel as of the date of publication. The specification is under continuous review, which can result in revisions based on changes in fuel, automotive requirements, or test methods, or a combination thereof. All users of this specification, therefore, should refer to the latest edition.

NOTE 1—If there is any doubt as to the latest edition of Specification D 4814, contact ASTM Headquarters.

1.6 Tests applicable to gasoline are not necessarily applicable to its blends with oxygenates. Consequently, the type of fuel under consideration must first be identified in order to select applicable tests. Test Method D 4815 provides a procedure for determining oxygenate concentration in mass percent. Test Method D 4815 also includes procedures for calculating mass oxygen content and oxygenate concentration in volume percent. Appendix X4 provides a procedure for calculating the mass oxygen content of a fuel using measured oxygenate type, oxygenate concentration in volume percent, and measured density or relative density of the fuel.

1.7 The test method in Annex A1 is state-of-the-art; however, it may be revised and eventually balloted for publication as a separate standard.

1.8 The values stated in SI units are the standard, except when other units are specified by federal regulation. Values given in parentheses are provided for information only.

NOTE 2—Many of the values shown in Table 1 were originally developed using U.S. customary units and were subsequently soft-converted to SI values. As a result, conversion of the SI values will sometimes differ slightly from the U.S. customary values shown because of round-off. In some cases, federal regulations specify non-SI units.

1.9 The following safety hazard caveat pertains only to the test method portion, Annex A1 of this specification. *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

² Available from ASTM Headquarters. Request RR:D02-1347.

¹ This specification is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.A on Gasoline and Oxygenated Fuels.

Current edition approved Dec. 10, 1995. Published February 1996. Originally published as D 4814 - 88. Last previous edition D 4814 - 95b.

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2. Referenced Documents

2.1 *ASTM Standards:*

- D 86 Test Method for Distillation of Petroleum Products³
- D 130 Test Method for Detection of Copper Corrosion from Petroleum Products by the Copper Strip Tarnish Test³
- D 287 Test Method for API Gravity of Crude Petroleum and Petroleum Products (Hydrometer Method)³
- D 381 Test Method for Existent Gum in Fuels by Jet Evaporation³
- D 439 Specification for Automotive Gasoline⁴
- D 525 Test Method for Oxidation Stability of Gasoline (Induction Period Method)³
- D 1266 Test Method for Sulfur in Petroleum Products (Lamp Method)³
- D 1298 Test Method for Density, Relative Density (Specific Gravity) or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method³
- D 2500 Test Method for Cloud Point of Petroleum Oils³
- D 2533 Test Method for Vapor-Liquid Ratio of Spark-Ignition Engine Fuels³
- D 2622 Test Method for Sulfur in Petroleum Products by X-Ray Spectrometry⁵
- D 2699 Test Method for Knock Characteristics of Motor Fuels by the Research Method⁶
- D 2700 Test Method for Knock Characteristics of Motor and Aviation Fuels by the Motor Method⁶
- D 2885 Test Method for Research and Motor Method Octane Ratings Using On-Line Analyzers⁶
- D 3120 Test Method for Trace Quantities of Sulfur in Light Liquid Petroleum Hydrocarbons by Oxidative Microcoulometry⁵
- D 3231 Test Method for Phosphorus in Gasoline⁴
- D 3237 Test Method for Lead in Gasoline by Atomic Absorption Spectrometry⁵
- D 3341 Test Method for Lead in Gasoline—Iodine Monochloride Method⁵
- D 4052 Test Method for Density and Relative Density of Liquids by Digital Density Meter⁵
- D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products⁵
- D 4306 Practice for Aviation Fuel Sample Containers for Tests Affected by Trace Contamination⁵
- D 4815 Test Method for Determination of MTBE, ETBE, TAME, DIPE, tertiary-Amyl Alcohol and C₁ to C₄ Alcohols in Gasoline by Gas Chromatography⁷
- D 4953 Test Method for Vapor Pressure of Gasoline and Gasoline-Oxygenate Blends (Dry Method)⁷
- D 5059 Test Methods for Lead in Gasoline by X-Ray Spectroscopy⁷
- D 5188 Test Method for Vapor-Liquid Ratio Temperature Determination of Fuels (Evacuated Chamber Method)⁷
- D 5190 Test Method for Vapor Pressure of Petroleum Products (Automatic Method)⁷

D 5191 Test Method for Vapor Pressure of Petroleum Products (Mini Method)⁷

D 5453 Test Method for the Determination of Total Sulfur in Light Hydrocarbons, Motor Fuels, and Oils by Ultraviolet Fluorescence⁷

D 5482 Test Method for Vapor Pressure of Petroleum Products (Mini Method-Atmospheric)⁷

E 1 Specification for ASTM Thermometers⁸

3. Terminology

3.1 *Definitions:*

3.1.1 *antiknock index, n*—the arithmetic average of the Research octane number (RON) and Motor octane number (MON), that is, (RON + MON)/2.

3.1.2 *gasoline, n*—a volatile mixture of liquid hydrocarbons, generally containing small amounts of additives, suitable for use as a fuel in spark-ignition, internal combustion engines.

3.1.3 *gasoline-alcohol blend, n*—a fuel consisting primarily of gasoline along with a substantial amount (more than 0.35 mass percent oxygen, or more than 0.15 mass percent oxygen if methanol is the only oxygenate) of one or more alcohols.

3.1.4 *gasoline-ether blend, n*—a fuel consisting primarily of gasoline along with a substantial amount (more than 0.35 mass percent oxygen) of one or more ethers.

3.1.5 *gasoline-oxygenate blend, n*—a fuel consisting primarily of gasoline along with a substantial amount (more than 0.35 mass percent oxygen, or more than 0.15 mass percent oxygen if methanol is the only oxygenate) of one or more oxygenates.

3.1.6 *oxygenate, n*—an oxygen-containing, ashless, organic compound, such as an alcohol or ether, which can be used as a fuel or fuel supplement.

3.2 *Applicability*—In order to determine when a fuel contains a substantial amount of an oxygenate, a gasoline-oxygenate blend is defined as a fuel which contains more than 0.35 mass percent oxygen, or more than 0.15 mass percent oxygen if methanol is the only oxygenate. The definitions in this section do not apply to fuels that contain an oxygenate as the primary component; for example, fuel methanol (M85).

NOTE 3—The criteria in 3.2 were selected with consideration given to current oxygenate levels in the marketplace, state labeling practices, and consistency with federal legislation and regulations.

NOTE 4—Refer to Test Method D 4815 to calculate the mass oxygen content of a fuel using oxygenate concentration in mass percent. Refer to Appendix X4 to calculate mass oxygen content of a fuel using oxygenate concentration in volume percent.

4. Ordering Information

4.1 The purchasing agency shall:

- 4.1.1 State the antiknock index as agreed upon with the seller,
- 4.1.2 Indicate the season and locality in which the fuel is to be used,
- 4.1.3 Indicate the lead level required (Table 3), and
- 4.1.4 State the concentration and types of oxygenates present as agreed upon with the seller.

⁸ *Annual Book of ASTM Standards*, Vol 14.03.

³ *Annual Book of ASTM Standards*, Vol 05.01.

⁴ Discontinued—See 1990 *Annual Book of ASTM Standards*, Vol 05.01.

⁵ *Annual Book of ASTM Standards*, Vol 05.02.

⁶ *Annual Book of ASTM Standards*, Vol 05.04.

⁷ *Annual Book of ASTM Standards*, Vol 05.03.

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TABLE 1 Vapor Pressure and Distillation Class Requirements

Vapor Pressure/ Distillation Class	Vapor Pressure, ^a max, kPa(ksi)	Distillation Temperatures, °C(°F), at % Evaporated ^b					Distillation Residue, vol %, max
		10 vol %, max	60 vol %		90 vol %, max	End Point, max	
			min	max			
AA	54(7.8)	70(158)	77(170)	121(250)	190(374)	225(437)	2
A	62(9.0)	70(158)	77(170)	121(250)	190(374)	225(437)	2
B	69(10.0)	85(149)	77(170)	118(245)	190(374)	225(437)	2
C	79(11.5)	80(140)	77(170)	118(240)	185(365)	225(437)	2
D	83(13.5)	55(131)	66(150)	113(235)	185(365)	225(437)	2
E	103(15.0)	50(122)	66(150)	110(230)	185(365)	225(437)	2

^a Consult EPA for approved test methods for compliance with EPA vapor pressure regulations.^b At 101.3 kPa pressure (760 mm Hg).

TABLE 2 Vapor Lock Protection Class Requirements

Vapor Lock Protection Class	Vapor/Liquid Ratio (V/L), ^{a,b}	
	Test Temperature, °C(°F)	V/L, max
1	60(140)	20
2	58(135)	20
3	51(124)	20
4	47(116)	20
5	41(105)	20

^a At 101.3 kPa pressure (760 mm Hg).^b The mercury confining fluid procedure of Test Method D 2533 shall be used for gasoline-oxygenate blends. Either glycerin or mercury confining fluid may be used for gasoline. Test Method D 5188 may be used for all fuels. The procedure for estimating temperature-V/L (see Appendix X2) may only be used for gasoline.

5. Performance Requirements

5.1 Some requirements and test methods applicable to automotive spark-ignition engine fuel depend on whether the fuel is a gasoline, or a gasoline-oxygenate blend. Test Method D 4815, a gas chromatographic test method, is the recommended procedure to detect the types and amounts of oxygenates. Once the type of fuel is known, the appropriate requirements and test methods can be identified by reference to Tables 1 and 2 and Section 7.

5.2 Volatility of fuels is varied for seasonal climatic changes and conformance to U.S. EPA volatility regulations by providing six vapor pressure/distillation classes and five vapor lock protection classes for fuel. Volatility of fuel is specified by an alphanumeric designation that uses a letter from Table 1 and a number from Table 2.

5.2.1 The seasonal and geographic distribution of the combined vapor pressure/distillation-vapor lock classes is shown in Table 4.

5.2.2 The EPA vapor pressure regulations can cause the distillation of the fuel to be less volatile, which for some vehicles, results in poorer warmup driveability performance.

5.2.3 Test Method D 2533 contains procedures for measuring temperature-V/L of both gasoline and gasoline-oxygenate blends. For gasoline-oxygenate blends, the procedure requires that mercury be used as the confining fluid in place of glycerin. Either confining fluid may be used for gasoline. Test Method D 5188 is an alternative method for determining vapor-liquid ratio temperatures by an evacuated chamber method for gasoline-oxygenate blends, as well as gasoline. In case of dispute, Test Method D 2533 is the referee method. The method for estimating temperature-V/L (see Appendix X2) is only applicable for gasoline.

5.3 Antiknock index (AKI) is very important to engine performance. The matching of engine octane requirement to fuel octane level (AKI) is critical to the durability and

performance of engines; this cannot be accomplished with a single specified minimum level of antiknock index. Appendix X1 includes a discussion of antiknock indexes of fuels currently marketed and relates these levels to the octane needs of broad groups of engines and vehicles. Also discussed is the effect of altitude and weather on vehicle antiknock requirements.

5.4 Additional fuel requirements are shown in Table 3.

5.5 The properties of gasoline-oxygenate blends can differ considerably from those of gasoline. Consequently, additional requirements are needed for gasoline-oxygenate blends. These requirements involve evaluation of compatibility with plastic and elastomeric materials in fuel systems, corrosion of metals, and especially in the case of gasoline-alcohol blends, water tolerance. Requirements for metal corrosion (other than copper) and material compatibility are not given because test methods and appropriate limits are still under development. When these have been developed they will be included in this specification. Water tolerance is specified in Table 5.

5.6 Depending on oxygenate type and concentration in the blend, vehicle driveability with gasoline-oxygenate blends can differ significantly from that with gasolines having similar volatility characteristics.

5.7 Water Tolerance:

5.7.1 The term water tolerance is used to indicate the ability of a gasoline-oxygenate blend to dissolve water without phase separation. This may not be a problem with gasoline-ether blends, but it is of primary concern for alcohol-containing blends, as blends of gasoline with low-molecular weight alcohols generally will dissolve about 0.1 to 0.7 mass % of water under normal conditions, depending on the nature and amount of the alcohol(s) used, the specific hydrocarbons present, and the temperature of the blend. When blends are exposed to a greater amount of water than they can dissolve, they separate into an alcohol-rich aqueous phase, the volume of which can be significantly greater than that of the additional water, and an alcohol-poor hydrocarbon phase. As the aqueous phase can be highly corrosive to many metals and the engine cannot operate on it, such separation is very undesirable. Blends containing low-molecular weight alcohols are generally hygroscopic and can eventually absorb enough moisture from ambient air to cause separation. The problem of phase separation can usually be avoided if the fuels are sufficiently water-free initially and care is taken during distribution to prevent contact with water. To help ensure this, gasoline-oxygenate blends shall be tested at the lowest temperatures to which they can be subjected, dependent on the time and place of intended use, as indicated in Table 5. The values in Table 5

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TABLE 3 Detailed Requirements for all Volatility Classes^a

Lead Content, max. g/L (g/U.S. gal) ^a		Copper Strip Corrosion, max	Solvent-washed Gum Content, mg/100 mL	Sulfur, max. mass %		Oxidation Stability, Minimum, minutes	Water Tolerance
Unleaded	Leaded			Unleaded	Leaded		
0.013(0.05)	1.1(4.2)	No. 1	5	0.10	0.16	240	c

^a See Appendix X1 for information on Antiknock Index.^b See Appendix X3 for U.S. EPA maximum limits for lead and phosphorus contents in unleaded gasoline (X3.2.1) and maximum average lead limits for leaded gasoline (X3.2.2).^c Water tolerance limits in terms of maximum temperature for phase separation are given in Table 5 (consult Annex A1).

are the 10th percentile 6-h minimum temperatures, with each reading specifically defined as the highest temperature of the six coldest consecutive hourly temperature readings of a 24-h day. For April through September (and occasionally October, and year-round for Hawaii), Table 5 specifies a minimum phase separation temperature of 10°C (50°F), even though the 10th percentile 6-h minimum temperature can be higher. Use of this temperature limit also reduces the risk of separation of the fuel in storage tanks where temperatures may be lower than ambient.

NOTE 5—The values in Table 5 are taken from the U.S. Army Belvoir Research Development and Engineering Center's Report No. 316, entitled "A Predictive Study for Defining Limiting Temperatures and Their Application in Petroleum Product Specifications." This can be obtained as Publication AD756-420 from the National Technical Information Service, Springfield, VA 22151.

5.7.2 The test procedure (see Annex A1) consists of cooling the fuel under specified conditions to the appropriate temperature listed in Table 5. It is important to note that when cooling to a low temperature some gasolines and many gasoline-oxygenate blends, especially those containing ethers, can take on a hazy appearance. This haze must be carefully distinguished from the test criterion described in Annex A1 of separation into two distinct phases with a more or less distinct common boundary, and must not be considered grounds for rejection of the fuel. This test also must not be confused with that described in Section 6, which is conducted at 21°C (70°F) or above, and for which the appearance of haze is proper grounds for rejection.

6. Workmanship

6.1 The finished fuel shall be visually free of undissolved water, sediment, and suspended matter; it shall be clear and bright at the ambient temperature or 21°C (70°F), whichever is higher.

6.2 Fuel to be used in this test shall not be cooled below about 15°C (59°F) or its temperature at the time the sample was taken, whichever is lower, as cooling of gasoline-oxygenate blends can produce changes in appearance that are not reversed on rewarming.

7. Test Methods

7.1 The requirements of this specification shall be determined in accordance with the methods listed below. Refer to the listed test methods to determine applicability or required modifications for use with gasoline-oxygenate blends.

7.1.1 *Distillation*—Test Method D 86.

7.1.2 *Vapor-Liquid Ratio*—Test Method D 2533 has procedures for determining vapor-liquid (V/L) ratios for both gasoline and gasoline-oxygenate blends. Because some oxygenates are miscible with the glycerin used in one procedure, another procedure using mercury as the confining fluid is

provided for gasoline-oxygenate blends. Either procedure may be used to determine V/L for gasoline. Test Method D 5188 is an evacuated chamber method for determining temperatures for vapor-liquid ratios between 8 to 1 and 75 to 1. It may be used for gasoline and gasoline-oxygenate blends.

7.1.3 *Vapor Pressure*—Test Methods D 4953, D 5190, D 5191, or D 5482.

7.1.4 *Corrosion, for Copper*, Test Method D 130, 3 h at 50°C (122°F).

7.1.5 *Solvent-Washed Gum Content*—Test Method D 381, air jet apparatus.

7.1.6 *Sulfur*—Test Methods D 1266, D 2622, D 3120, or D 5453. With Test Method D 3120, fuels with sulfur content greater than 100 ppm (0.0100 mass %) must be diluted with isooctane. The dilution of the sample may result in a loss of precision. Test Method D 3120 cannot be used when the lead concentration is greater than 0.4 g/L (1.4 g/U.S. gal).

7.1.7 *Lead*—Test Methods D 3341 or D 5059 (Test Methods A or B). For lead levels below 0.03 g/L (0.1 g/U.S. gal) use Test Methods D 3237 or D 5059 (Test Method C).

7.1.8 *Oxidation Stability*—Test Method D 525.

7.1.9 *Oxygenate Detection*—Test Method D 4815 is designed for the quantitative determination of methyl *tert*-butyl ether (MTBE), ethyl *tert*-butyl ether (ETBE), *tert*-amyl methyl ether (TAME), diisopropylether, methyl alcohol, ethyl alcohol, isopropyl alcohol, *n*-propyl alcohol, isobutyl alcohol, *tert*-butyl alcohol, sec-butyl alcohol, *n*-butyl alcohol, and *tert*-amyl alcohol. Results are reported in mass percent, but Test Method D 4815 includes procedures for calculating oxygenate concentration in volume percent and mass oxygen content using mass percent oxygenate results.

7.1.10 *Water Tolerance*—See Annex A1 for a test method.

8. Precision and Bias

8.1 The precision of each required test method with gasoline is included in the standard applicable to each method. In many cases, the precision applicable to gasoline-oxygenate blends has not been established yet.

9. Keywords

9.1 alcohol; antiknock index; automotive fuel; automotive gasoline; automotive spark-ignition engine fuel; copper strip corrosion; corrosion; distillation; driveability; EPA regulations; ethanol; ether; fuel; gasoline; gasoline-alcohol blend; gasoline-ethanol blend; gasoline-ether blend; gasoline-oxygenate blend; induction period; lead; leaded fuel; methanol; MTBE; octane number; octane requirement; oxidation stability; oxygenate; oxygenate detection; phase separation; phosphorous; solvent-washed gum; sulfur; $T_{V/L}$ = 20; unleaded fuel; vapor-liquid ratio; vapor lock; vapor pressure; volatility; water tolerance

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TABLE 4 Schedule of Seasonal and Geographical Volatility Classes⁴

This schedule, subject to agreement between purchaser and seller, denotes the volatility properties of the fuel at the time and place of bulk delivery to the fuel dispensing facilities for the end user. For Sept. 16 through April 30 (the time period not covered by EPA Phase II vapor pressure requirements), volatility properties for the previous month or the current month are acceptable for the end user from the 1st through the 15th day of the month. From the 16th day through the end of the month, volatility properties of the fuel delivered to the end user shall meet the requirements of the specified class(es). To ensure compliance with EPA Phase II vapor pressure requirements, vapor pressure for finished gasoline tankage at refineries, importers, pipelines, and terminals during May and for the entire distribution system, including retail stations, from June 1 to Sept. 15 shall meet only the current month's class. Shipments should anticipate this schedule.

Where alternative classes are listed, either class or intermediate classes are acceptable; the option shall be exercised by the seller.

State	Jan.	Feb.	Mar.	Apr.	May ^a	June	July	Aug.	Sept. 1-15	Sept. 16-30	Oct.	Nov.	Dec.
Alabama	D-4	D-4	D-4/C-3	C-3/A-3	A-3 (C-3)	A-3 ^D	A-3 ^D	A-2 ^E	A-2 ^E	A-2/C-3	C-3	C-3/D-4	D-4
Alaska	E-5	E-5	E-5	E-5	E-5/D-4	D-4	D-4	D-4	D-4	D-4/E-5	E-5	E-5	E-5
Arizona													
N 34° Latitude and E 111° Longitude	D-4	D-4	D-4/C-3	C-3/A-2	A-2 (B-2)	A-1	A-1	A-1	A-2	A-2/B-2	B-2/C-3	C-3/D-4	D-4
Remainder of State	D-4	D-4/C-3	C-3/B-2	B-2/A-2	A-2 (B-2)	A-1 ^F	A-1 ^F	A-1 ^F	A-1 ^E	A-1	A-1/B-2	B-2/C-3	C-3/D-4
Arkansas	E-5/D-4	D-4	D-4/C-3	C-3/A-3	A-3 (C-3)	A-3	A-2	A-2	A-2	A-2/C-3	C-3/D-4	D-4	D-4/E-5
California:													
North Coast	E-5/D-4	D-4	D-4	D-4/A-3	A-3 (C-3)	A-3 ^D	A-2 ^E	A-2 ^E	A-2 ^E	A-2/B-2	B-2/C-3	C-3/D-4	D-4/E-5
South Coast	D-4	D-4	D-4/C-3	C-3/A-3	A-3 (C-3)	A-2 ^E	A-2 ^E	A-2 ^E	A-2 ^E	A-2/B-2	B-2/C-3	C-3/D-4	D-4
Southeast	D-4	D-4/C-3	C-3/B-2	B-2/A-2	A-2 (B-2)	A-1 ^F	A-1 ^F	A-1 ^F	A-1 ^F	A-1	A-1/B-2	B-2/C-3	C-3/D-4
Interior	E-5/D-4	D-4	D-4	D-4/A-3	A-3 (C-3)	A-2 ^E	A-2 ^E	A-2 ^E	A-2 ^E	A-2/B-2	B-2/C-3	C-3/D-4	D-4/E-5
Colorado	E-5	E-5/D-4	D-4/C-3	C-3/A-3	A-3 (C-3)	A-2 ^E	A-2 ^E	A-2 ^E	A-2 ^E	A-2/B-2	B-2/C-3	C-3/D-4	D-4/E-5
Connecticut	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3	A-3	A-3	A-3	A-3/D-4	D-4	D-4/E-5	E-5
Delaware	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3	A-3	A-3	A-3	A-3/D-4	D-4	D-4/E-5	E-5
District of Columbia	E-5	E-5/D-4	D-4	D-4/A-3	A-3 (C-3)	A-3 ^D	A-3 ^D	A-3 ^D	A-3 ^D	A-3/C-3	C-3/D-4	D-4/E-5	E-5
Florida	D-4	D-4	D-4/C-3	C-3/A-3	A-3 (C-3)	A-3 ^D	A-3 ^D	A-3 ^D	A-3 ^D	A-3/C-3	C-3	C-3/D-4	D-4
Georgia	D-4	D-4	D-4/C-3	C-3/A-3	A-3 (C-3)	A-3 ^D	A-3 ^D	A-2 ^E	A-2 ^E	A-2/C-3	C-3	C-3/D-4	D-4
Hawaii	C-3	C-3	C-3	C-3	C-3	C-3	C-3	C-3	C-3	C-3	C-3	C-3	C-3
Idaho:													
N 48° Latitude	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3	A-2	A-2	A-2	A-2/C-3	C-3/D-4	D-4/E-5	E-5
S 48° Latitude	E-5	E-5/D-4	D-4	D-4/A-3	A-3 (C-3)	A-2	A-2	A-2	A-2	A-2/B-2	B-2/C-3	C-3/D-4	D-4/E-5
Illinois:													
N 40° Latitude	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3	A-3	A-3	A-3	A-3/C-3	C-3/D-4	D-4/E-5	E-5
S 40° Latitude	E-5	E-5	E-5/D-4	D-4/A-3	A-3 (C-3)	A-3	A-3	A-3	A-3	A-3/C-3	C-3/D-4	D-4	D-4/E-5
Indiana	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3	A-3	A-3	A-3	A-3/C-3	C-3/D-4	D-4/E-5	E-5
Iowa	E-5	E-5	E-5/D-4	D-4/A-3	A-3 (C-3)	A-3	A-3	A-3	A-3	A-3/C-3	C-3/D-4	D-4/E-5	E-5
Kansas	E-5	E-5/D-4	D-4/C-3	C-3/A-3	A-3 (C-3)	A-2 ^E	A-2 ^E	A-2 ^E	A-2 ^E	A-2/B-2	B-2/C-3	C-3/D-4	D-4/E-5
Kentucky	E-5	E-5/D-4	D-4	D-4/A-3	A-3 (C-3)	A-3	A-3	A-3	A-3	A-3/C-3	C-3/D-4	D-4/E-5	E-5
Louisiana	D-4	D-4	D-4/C-3	C-3/A-3	A-3 (C-3)	A-3 ^D	A-3 ^D	A-2 ^E	A-2 ^E	A-2/C-3	C-3	C-3/D-4	D-4
Maine	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3	A-3	A-3	A-3	A-3/D-4	D-4	D-4/E-5	E-5
Maryland	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3 ^D	A-3 ^D	A-3 ^D	A-3 ^D	A-3/C-3	C-3/D-4	D-4/E-5	E-5
Massachusetts	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3	A-3	A-3	A-3	A-3/D-4	D-4	D-4/E-5	E-5
Michigan	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3	A-3	A-3	A-3	A-3/D-4	D-4	D-4/E-5	E-5
Minnesota	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3	A-3	A-3	A-3	A-3/C-3	C-3/D-4	D-4/E-5	E-5
Mississippi	D-4	D-4	D-4/C-3	C-3/A-3	A-3 (C-3)	A-3	A-2	A-2	A-2	A-2/C-3	C-3	C-3/D-4	D-4
Missouri	E-5	E-5/D-4	D-4	D-4/A-3	A-3 (C-3)	A-3 ^D	A-2 ^E	A-2 ^E	A-2 ^E	A-2/C-3	C-3/D-4	D-4	D-4/E-5
Montana	E-5	E-5	E-5/D-4	D-4/A-3	A-3 (C-3)	A-2	A-2	A-2	A-2	A-2/C-3	C-3/D-4	D-4/E-5	E-5
Nebraska	E-5	E-5	E-5/D-4	D-4/A-3	A-3 (C-3)	A-2	A-2	A-2	A-2	A-2/B-2	B-2/C-3	C-3/D-4	D-4/E-5
Nevada:													
N 38° Latitude	E-5	E-5/D-4	D-4	D-4/A-3	A-3 (C-3)	A-2 ^E	A-2 ^E	A-2 ^E	A-2 ^E	A-2/B-2	B-2/C-3	C-3/D-4	D-4/E-5
S 38° Latitude	D-4	D-4/C-3	C-3/B-2	B-2/A-2	A-2 (B-2)	A-1	A-1	A-1	A-1	A-1/B-2	B-2/C-3	C-3/D-4	D-4
New Hampshire	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3	A-3	A-3	A-3	A-3/D-4	D-4	D-4/E-5	E-5
New Jersey	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3	A-3	A-3	A-3	A-3/D-4	D-4	D-4/E-5	E-5
New Mexico:													
N 34° Latitude	E-5/D-4	D-4	D-4/C-3	C-3/A-2	A-2 (B-2)	A-1	A-1	A-2	A-2	A-2/B-2	B-2/C-3	C-3/D-4	D-4
S 34° Latitude	D-4	D-4/C-3	C-3/B-2	B-2/A-2	A-2 (B-2)	A-1	A-1	A-1	A-1	A-1/B-2	B-2/C-3	C-3/D-4	D-4
New York	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3	A-3	A-3	A-3	A-3/D-4	D-4	D-4/E-5	E-5
North Carolina	E-5/D-4	D-4	D-4	D-4/A-3	A-3 (C-3)	A-3 ^D	A-3 ^D	A-2 ^E	A-2 ^E	A-2/C-3	C-3/D-4	D-4	D-4/E-5
North Dakota	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3	A-2	A-2	A-2	A-2/C-3	C-3/D-4	D-4/E-5	E-5
Ohio	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3	A-3	A-3	A-3	A-3/C-3	C-3/D-4	D-4/E-5	E-5
Oklahoma	E-5/D-4	D-4	D-4/C-3	C-3/A-3	A-3 (C-3)	A-2	A-2	A-2	A-2	A-2/B-2	B-2/C-3	C-3/D-4	D-4/E-5
Oregon:													
E 122° Longitude	E-5	E-5/D-4	D-4	D-4/A-4	A-4 (D-4)	A-3	A-2	A-2	A-2	A-2/C-3	C-3/D-4	D-4	D-4/E-5
W 122° Longitude	E-5	E-5/D-4	D-4	D-4/A-4	A-4 (D-4)	A-3 ^D	A-3 ^D	A-3 ^D	A-3 ^D	A-3/C-3	C-3/D-4	D-4/E-5	E-5
Pennsylvania	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3	A-3	A-3	A-3	A-3/D-4	D-4	D-4/E-5	E-5
Rhode Island	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3	A-3	A-3	A-3	A-3/D-4	D-4	D-4/E-5	E-5
South Carolina	D-4	D-4	D-4	D-4/A-3	A-3 (C-3)	A-3	A-3	A-2	A-2	A-2/C-3	C-3/D-4	D-4	D-4
South Dakota	E-5	E-5	E-5/D-4	D-4/A-3	A-3 (C-3)	A-2	A-2	A-2	A-2	A-2/B-2	B-2/C-3	C-3/D-4	D-4/E-5
Tennessee	E-5/D-4	D-4	D-4	D-4/A-3	A-3 (C-3)	A-3 ^D	A-3 ^D	A-2 ^E	A-2 ^E	A-2/C-3	C-3/D-4	D-4	D-4/E-5
Texas:													
E 99° Longitude	D-4	D-4	D-4/C-3	C-3/A-3	A-3 (C-3)	A-3 ^D	A-2 ^E	A-2 ^E	A-2 ^E	A-2/B-2	B-2/C-3	C-3/D-4	D-4
W 99° Longitude	D-4	D-4/C-3	C-3/B-2	B-2/A-2	A-2 (B-2)	A-1 ^F	A-1 ^F	A-1 ^F	A-1 ^F	A-1/B-2	B-2/C-3	C-3/D-4	D-4
Utah	E-5	E-5/D-4	D-4	D-4/A-3	A-3 (C-3)	A-2 ^E	A-2 ^E	A-2 ^E	A-2 ^E	A-2/B-2	B-2/C-3	C-3/D-4	D-4/E-5
Vermont	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3	A-3	A-3	A-3	A-3/D-4	D-4	D-4/E-5	E-5
Virginia	E-5	E-5/D-4	D-4	D-4/A-3	A-3 (C-3)	A-3 ^D	A-3 ^D	A-3 ^D	A-3 ^D	A-3/C-3	C-3/D-4	D-4/E-5	E-5



TABLE 4 (Continued)

State	Jan.	Feb.	Mar.	Apr.	May ^a	June	July	Aug.	Sept. 1-15	Sept. 16-30	Oct.	Nov.	Dec.
Washington:													
E 122° Longitude	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3	A-2	A-2	A-2	A-2/C-3	C-3/D-4	D-4/E-5	E-5
W 122° Longitude	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3	A-3	A-3	A-3	A-3/C-3	C-3/D-4	D-4/E-5	E-5
West Virginia	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3	A-3	A-3	A-3	A-3/C-3	C-3/D-4	D-4/E-5	E-5
Wisconsin	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3	A-3	A-3	A-3	A-3/C-3	C-3/D-4	D-4/E-5	E-5
Wyoming	E-5	E-5	E-5/D-4	D-4/A-3	A-3 (C-3)	A-2	A-2	A-2	A-2	A-2/B-2	B-2/C-3	C-3/D-4	D-4/E-5

^a For the period May 1 through September 15, the specified vapor pressure classes comply with 1992 U.S. EPA Phase II volatility regulations. EPA regulations allow 1.0 psi higher vapor pressure for gasoline-ethanol blends containing 8 to 10 vol % ethanol for the same period. See Appendix X3 for additional federal volatility regulations.

^b Values in parentheses are permitted for retail stations and other end users.

^c Details of State Climatological Division by county as indicated:

California, North Coast—Alameda, Contra Costa, Del Norte, Humboldt, Lake, Marin, Mendocino, Monterey, Napa, San Benito, San Francisco, San Mateo, Santa Clara, Santa Cruz, Solano, Sonoma, Trinity

California, Interior—Lassen, Modoc, Plumas, Sierra, Siskiyou, Alpine, Amador, Butte, Calaveras, Colusa, El Dorado, Fresno, Glenn, Kern (except that portion lying east of Los Angeles County Aqueduct), Kings, Madera, Mariposa, Maricopa, Placer, Sacramento, San Joaquin, Shasta, Stanislaus, Sutter, Tehama, Tulare, Tuolumne, Yolo, Yuba, Nevada

California, South Coast—Orange, San Diego, San Luis Obispo, Santa Barbara, Ventura, Los Angeles (except that portion north of the San Gabriel Mountain range and east of the Los Angeles County Aqueduct)

California, Southeast—Imperial, Riverside, San Bernardino, Los Angeles (that portion north of the San Gabriel Mountain range and east of the Los Angeles County Aqueduct), Mono, Inyo, Kern (that portion lying east of the Los Angeles County Aqueduct)

^d AA-3 for the following ozone nonattainment areas:

(See Federal Register 56, 215, 58684, November 6, 1991, for description of the geographic boundary for each area.)

Alabama—Birmingham
California—Monterey Bay
California—San Francisco-Bay Area
District of Columbia—Washington
Florida—Jacksonville
Florida—Miami-Fort Lauderdale-West Palm Beach
Florida—Tampa-St. Petersburg-Clearwater
Georgia—Atlanta
Louisiana—Baton Rouge
Louisiana—Beauregard Parish
Louisiana—Grant Parish
Louisiana—Lafayette
Louisiana—Lafourche Parish
Louisiana—Lake Charles
Louisiana—New Orleans
Louisiana—St. James Parish
Louisiana—St. Mary Parish
Maryland—Baltimore
Maryland—Kent and Queen Anne's Counties
Maryland—Philadelphia-Wilmington-Trenton Area

Maryland—Washington Area
Missouri—Kansas City
Missouri—St. Louis
North Carolina—Charlotte-Gastonia
North Carolina—Greensboro-Winston Salem-High Point
North Carolina—Raleigh-Durham
Oregon—Portland-Vancouver AQMA
Oregon—Salem
Tennessee—Memphis
Tennessee—Nashville
Texas—Beaumont-Port Arthur
Texas—Dallas-Fort Worth
Texas—Houston-Galveston-Brazoria
Texas—Victoria
Virginia—Norfolk-Virginia Beach-Newport News
Virginia—Richmond
Virginia—Smyth County
Virginia—Washington Area

^e AA-2 for the following ozone nonattainment areas:

(See Federal Register 56, 215, 58694, November 6, 1991, for description of the geographic boundary for each area.)

Alabama—Birmingham
Arizona—Phoenix
California—Chico
California—Los Angeles-South Coast Air Basin
California—Monterey Bay
California—Sacramento Metro
California—San Diego
California—San Francisco-Bay Area
California—San Joaquin Valley
California—Santa Barbara-Santa Maria-Lompoc
California—Ventura County
California—Yuba City
Colorado—Denver-Boulder
Georgia—Atlanta
Kansas—Kansas City
Louisiana—Baton Rouge
Louisiana—Beauregard Parish
Louisiana—Grant Parish
Louisiana—Lafayette
Louisiana—Lafourche Parish

Louisiana—Lake Charles
Louisiana—New Orleans
Louisiana—St. James Parish
Louisiana—St. Mary Parish
Missouri—Kansas City
Missouri—St. Louis
Nevada—Reno
North Carolina—Charlotte-Gastonia
North Carolina—Greensboro-Winston Salem-High Point
North Carolina—Raleigh-Durham
Tennessee—Memphis
Tennessee—Nashville
Texas—Beaumont-Port Arthur
Texas—Dallas-Fort Worth
Texas—Houston-Galveston-Brazoria
Texas—Victoria
Utah—Salt Lake City

^f AA-1 for the following ozone nonattainment areas:

(See Federal Register 56, 215, 58684, November 6, 1991, for description of the geographic boundary for each area.)

Arizona—Phoenix
California—Imperial County
California—Southeast Desert Modified AQMA
Texas—El Paso

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TABLE 5 Maximum Temperature for Phase Separation, °C^a

Temperature Conversion °F = (°C × 1.8) + 32°												
State	Jan.	Feb.	March	April	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
Alabama	-4	-3	0	5	10	10	10	10	10	6	0	-4
Alaska:												
Southern Region	-27	-26	-23	-11	1	7	9	7	1	-9	-19	-23
South Mainland	-41	-39	-31	-14	-1	7	9	5	-2	-18	-32	-41
N of 62° Latitude												
Arizona:												
N of 34° Latitude	-11	-7	-7	-2	2	6	10	10	6	1	-8	-9
S of 34° Latitude	-2	-1	2	7	10	10	10	10	10	9	2	-1
Arkansas	-9	-6	-2	6	10	10	10	10	10	4	-2	-6
California:												
North Coast	-2	0	1	4	6	8	9	9	8	8	2	-2
South Coast	-2	-1	2	4	7	9	10	10	9	6	1	-2
Southeast	-7	-3	-1	3	8	10	10	10	9	4	-3	-6
Interior	-4	-3	-3	-1	3	8	10	10	10	6	0	-2
Colorado:												
E of 105° Longitude	-14	-12	-9	-3	4	10	10	10	7	1	-8	-11
W of 105° Longitude	-24	-20	-12	-6	-1	4	8	8	1	-8	-14	-21
Connecticut	-14	-13	-8	-1	5	10	10	10	7	1	-4	-12
Delaware	-9	-8	-3	0	8	10	10	10	10	4	-1	-8
District Columbia	-8	-7	-3	3	9	10	10	10	10	5	0	-7
Florida:												
N of 29° Latitude	-1	1	4	9	10	10	10	10	10	9	3	-1
S of 29° Latitude	4	7	8	10	10	10	10	10	10	10	9	5
Georgia	-5	-2	1	6	10	10	10	10	10	6	0	-3
Hawaii	10	10	10	10	10	10	10	10	10	10	10	10
Idaho	-17	-16	-11	-3	-5	4	10	8	3	-2	-11	-15
Illinois:												
N of 40° Latitude	-18	-16	-9	-1	4	10	10	10	7	1	-7	-16
S of 40° Latitude	-15	-12	-7	1	7	10	10	10	9	3	-6	-13
Indiana	-16	-13	-7	-1	4	10	10	10	7	1	-6	-14
Iowa	-23	-19	-13	-3	4	10	10	10	6	0	-12	-20
Kansas	-17	-12	-8	-3	5	10	10	10	7	0	-8	-13
Kentucky	-12	-9	-4	1	8	10	10	10	9	3	-4	-11
Louisiana	-3	0	3	8	10	10	10	10	10	7	2	-1
Maine	-24	-22	-16	-4	1	7	10	8	3	-2	-8	-20
Maryland	-9	-8	-3	3	9	10	10	10	10	4	-2	-8
Massachusetts	-15	-14	-7	-1	4	10	10	10	6	0	-4	-13
Michigan:												
Lower Michigan	-18	-17	-12	-3	1	7	10	9	5	0	-6	-14
Upper Michigan	-21	-20	-15	-6	-1	6	9	9	4	-1	-9	-18
Minnesota	-31	-28	-20	-7	0	8	10	8	1	-3	-16	-28
Mississippi	-3	-1	2	7	10	10	10	10	10	7	1	-3
Missouri	-14	-11	-6	1	8	10	10	10	10	3	-6	-12
Montana	-28	-24	-19	-6	1	6	9	8	1	-5	-17	-23
Nebraska	-19	-14	-11	-3	4	9	10	10	5	-2	-10	-16
Nevada:												
N of 38° Latitude	-18	-13	-8	-3	1	5	9	7	2	-3	-11	-14
S of 38° Latitude	-8	-5	-1	1	9	10	10	10	10	4	-3	-6
New Hampshire	-18	-17	-9	-2	3	9	10	9	3	-1	-6	-16
New Jersey	-10	-9	-4	2	7	10	10	10	10	4	-1	-8
New Mexico:												
N of 34° Latitude	-14	-11	-7	-2	1	7	10	10	7	1	-8	-12
S of 34° Latitude	-7	-5	-1	6	10	10	10	10	10	7	-2	-5
New York:												
N of 42° Latitude	-21	-20	-13	-3	2	9	10	10	4	-1	-6	-18
S of 42° Latitude	-13	-13	-7	1	8	10	10	10	8	2	-3	-12
North Carolina	-9	-7	-3	1	7	10	10	10	8	1	-5	-8
North Dakota	-29	-27	-11	-6	1	8	10	10	3	-2	-17	-24
Ohio	-14	-13	-8	-2	6	10	10	10	7	1	-6	-13
Oklahoma	-12	-8	-5	1	7	10	10	10	10	4	-4	-9
Oregon:												
E of 122° Longitude	-17	-12	-6	-3	0	4	6	6	2	-3	-8	-12
W of 122° Longitude	-5	-3	-1	2	5	8	10	10	7	2	-3	-3
Pennsylvania:												
N of 41° Latitude	-17	-19	-13	-4	1	6	9	8	2	-1	-6	-16
S of 41° Latitude	-13	-14	-9	-1	5	10	10	10	7	2	-4	-12
Rhode Island	-11	-11	-5	1	6	10	10	10	8	3	-2	-10
South Carolina	-3	-2	0	6	10	10	10	10	10	7	1	-3
South Dakota	-24	-21	-16	-4	3	10	10	10	4	-2	-12	-21
Tennessee	-9	-7	-3	2	9	10	10	10	10	2	-3	-8

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TABLE 5 Continued

Temperature Conversion °F = (°C × 1.8) + 32°												
State	Jan.	Feb.	March	April	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
Texas:												
N of 31° Latitude	-11	-8	-4	2	8	10	10	10	10	6	-3	-7
S of 31° Latitude	-1	1	4	10	10	10	10	10	10	10	3	1
Utah	-15	-11	-7	-2	2	8	10	10	7	2	-11	-12
Vermont	-20	-21	-12	-2	2	8	10	10	6	0	-6	-17
Virginia	-8	-7	-3	3	9	10	10	10	10	4	-2	-7
Washington:												
E of 122° Longitude	-13	-6	-3	1	4	7	10	10	7	1	-6	-7
W of 122° Longitude	-6	-2	-2	1	4	7	8	9	6	2	-2	-2
West Virginia	-13	-12	-7	-2	4	8	10	10	5	-2	-7	-12
Wisconsin	-25	-21	-15	-3	3	8	10	10	5	-1	-11	-21
Wyoming	-23	-17	-14	-6	0	5	10	10	3	-2	-13	-16

^a A maximum phase separation temperature of 10°C (50°F) is specified, even if the 6-h 10th percentile minimum temperature for the area and month can be higher.

^b The designated areas of Alaska are divided as follows:

Southern Region—The Aleutians, Kodiak Island, the coastal strip East of Longitude 141°, and the Alaskan Peninsula South of Latitude 62°.

South Mainland—The portion of Alaska South of Latitude 62°, except the Southern Region.

North of Latitude 62°—The specification test temperature must be agreed between the vendor and purchaser having regard to equipment design, expected weather conditions, and other relevant factors.

^c The designated areas of California are divided by county as follows:

North Coast—Alameda, Contra Costa, Del Norte, Humboldt, Lake, Marin, Mendocino, Monterey, Napa, San Benito, San Francisco, San Mateo, Santa Clara, Santa Cruz, Solano, Sonoma, Trinity.

Interior—Lassen, Modoc, Plumas, Sierra, Siskiyou, Alpine, Amador, Butte, Calaveras, Colusa, El Dorado, Fresno, Glenn, Kern (excepting that portion lying east of the Los Angeles County Aqueduct), Kings, Madera, Mariposa, Merced, Placer, Sacramento, San Joaquin, Shasta, Stanislaus, Sutter, Tehama, Tulare, Tuolumne, Yolo, Yuba, Nevada.

South Coast—Orange, San Diego, San Luis Obispo, Santa Barbara, Ventura, Los Angeles (except that portion lying north of the San Gabriel Mountain range and east of the Los Angeles County Aqueduct).

Southeast—Imperial, Riverside, San Bernardino, Los Angeles (that portion lying north of the San Gabriel Mountain range and east of the Los Angeles County Aqueduct), Mono, Inyo, Kern (that portion lying east of the Los Angeles County Aqueduct).

^d The designated areas of Michigan are divided as follows:

Lower Michigan—That portion of the state lying East of Lake Michigan.

Upper Michigan—That portion of the state lying North of Wisconsin and of Lake Michigan.

ANNEX

(Mandatory Information)

A1. TEST METHOD FOR WATER TOLERANCE (PHASE SEPARATION) OF SPARK-IGNITION ENGINE FUEL

A1.1 Scope

A1.1.1 This test method determines the ability of gasoline-oxygenate blends to retain water in solution or in a stable suspension at the lowest temperature to which they are likely to be exposed in use.

A1.1.2 The values stated in SI units are standard.

A1.1.3 This test method is state-of-the-art; however, it may be revised and eventually balloted for publication as a separate standard.

A1.2 Summary of Test Method

A1.2.1 The sample of fuel is cooled at a controlled rate to its expected use temperature and is periodically observed for both haze and phase separation. The apparatus of Test Method D 2500 or a dry ice-isopropyl alcohol bath may be used. A maximum cooling rate of 2°C (4°F)/min is specified because phase separation in gasoline-oxygenate blends has a relatively long but unpredictable induction period.

A1.3 Significance and Use

A1.3.1 Some oxygenate-containing fuels, and gasoline-alcohol blends in particular have a very limited ability to retain water in solution or in stable suspension, and if the

amount of water in the blend exceeds this limit, the fuel will separate into a lower oxygenate-rich aqueous phase and an upper oxygenate-lean hydrocarbon phase. The most important factor governing the ability of a specific fuel to retain water without such separation is its temperature. This method is intended to determine the maximum temperature at which the fuel will separate. The 10th percentile 6-h minimum temperature, or 10°C (50°F) whichever is lower, for the time of year and geographic area of the United States in which the fuel may be used, are tabulated in Table 3 of Specification D 4814. The temperatures represent the maximum temperatures above which the fuel must not separate into two distinct phases.

A1.3.2 Note that in this test, actual separation of the sample into two distinct phases is the criterion for failure. The following are indications of phase separation:

A1.3.2.1 The formation of droplets large enough to be detected by the unaided eye. They can be either clinging to the sides of the container or collect on the bottom.

A1.3.2.2 The formation of two layers separated by either a common boundary, or a layer of emulsion.

A1.3.3 Formation of haze without one of these indications of separation is not cause for rejection.

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A1.4 Apparatus

A1.4.1 Test Container—The container may be as specified in the apparatus section of Test Method D 2500, but any glass container of about 100 mL capacity may be used. This container may be marked at the level of 40 mL.

A1.4.2 Thermometers, meeting the requirements of Specification E 1. ASTM thermometer 6C (range -80 to $+20^{\circ}\text{C}$, 1°C graduations, 76 mm immersion. Thermometer 6F is the Fahrenheit equivalent of 6C) spans the necessary range of temperatures. A thermometer must be provided for each container, mounted to pass through the stopper.

A1.4.3 Viton Rubber Stopper—to fit sample container, bored centrally for the test thermometer.

A1.4.4 Cooling Bath—May be of similar dimensions to those specified in 6.7 of Test Method D 2500 and provided with a jacket, disk, and gasket as specified in the apparatus section, filled with an equal-volume mixture of water and “permanent” antifreeze and provided with refrigeration coils capable of reducing its temperature to -40°C (-40°F). Alternatively, a dry ice-isopropyl alcohol bath may be used.

A1.5 Sampling and Handling

A1.5.1 Draw samples in accordance with the instructions in Practice D 4057, specifically 7.8.3, 7.9.1, and 10.3, except that water displacement, 10.3.1.8, shall not be used.

A1.5.2 Draw the samples in steel cans that have been solvent washed in accordance with 6.3.3.1 of Practice D 4306.

A1.5.3 Store the samples in a refrigerator (2 to 7°C , 35 to 45°F) whenever not actually transferring sample.

A1.5.4 Because gasoline-alcohol blends are hygroscopic as well as volatile, minimize contact with the atmosphere by keeping sample containers tightly closed except when transferring sample.

A1.6 Procedure

A1.6.1 Warm the sample to 15°C (59°F) and shake, to redissolve any water that may have settled out at the refrigerator temperature.

A1.6.2 Cool the test containers to 10 to 15°C (50 to 59°F). Carry out steps A1.6.3 through A1.6.5 as promptly as possible to minimize vaporization losses and absorption of water from the atmosphere.

A1.6.3 Rinse out the cooled test container with some of the sample to be tested. Drain.

A1.6.4 Pour about 40 mL of the sample into the test

container. The precise amount is not critical, but it must be enough to submerge the thermometer bulb adequately, without being so much as to require an excessive amount of cooling time. If the sample has separated, as defined in A1.3.2, terminate the test.

A1.6.5 Seal the test container with the rubber stopper. Locate the thermometer bulb approximately at the center of the fuel sample.

A1.6.6 Cool the sample by intermittent immersion in or circulation of the coolant. The sample is not to be swirled or shaken while in the cooling bath. Starting at a cooling bath temperature not higher than 10°C (50°F), or 16°C (30°F) above the test temperature, cool the sample at a maximum rate of 2°C (4°F)/minute until phase separation occurs, or the test temperature is reached.

A1.6.7 At 2°C (4°F) intervals, remove the test container from the cooling bath and shake vigorously for 5 to 10 s. Wipe the exterior of the sample container with a towel moistened with isopropyl alcohol to remove any condensation, and observe the condition of the sample for no more than 5 s against a light colored, illuminated background.

A1.6.8 It is likely that the sample will get hazy prior to actual phase separation as defined in A1.3.2. Record the sample temperature at the first indication of haze (when cooling); and the temperature when the haze disappears (warming).

A1.6.9 Record the temperature of phase separation (A1.3.2). Then allow the sample to warm at ambient temperature. Shake the sample vigorously after a temperature rise of 2°C (4°F), and observe. Record a “warming” phase recombination temperature, and haze disappearance temperature. Average these “cooling” and “warming” temperatures to determine the actual phase separation and haze point temperatures. Repeat this process for improved accuracy.

A1.7 Report

A1.7.1 Report the following information:

A1.7.1.1 Report the averaged haze point and phase separation temperatures found in A1.6.9.

A1.8 Precision and Bias

A1.8.1 Precision—The precision of this test method has not been determined.

A1.8.2 Bias—There being no criteria for measuring bias in these test-product combinations, no statement of bias can be made.

APPENDIXES**(Nonmandatory Information)****X1. SIGNIFICANCE OF ASTM SPECIFICATION FOR AUTOMOTIVE SPARK-IGNITION ENGINE FUEL****X1.1 General**

X1.1.1 Antiknock rating and volatility define the general characteristics of automotive spark-ignition engine fuel. Other characteristics relate to the following: limiting the concentration of undesirable components so that they will not adversely affect engine performance and ensuring the stability of fuel as well as its compatibility with materials

used in engines and their fuel systems.

X1.1.2 Fuel for spark-ignition engines is a complex mixture composed of relatively volatile hydrocarbons that vary widely in their physical and chemical properties and may contain oxygenates. Fuel is exposed to a wide variety of mechanical, physical, and chemical environments. Thus, the properties of fuel must be balanced to give satisfactory

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engine performance over an extremely wide range of operating conditions. The prevailing standards for fuel represent compromises among the numerous quality and performance requirements. This ASTM specification is established on the basis of the broad experience and close cooperation of producers of fuel, manufacturers of automotive equipment, and users of both.

X1.2 Engine Knock

X1.2.1 The fuel-air mixture in the cylinder of a spark-ignition engine will, under certain conditions, autoignite in localized areas ahead of the flame front that is progressing from the spark. This is engine spark knock which can cause a ping that may be audible to the customer.

X1.2.2 The antiknock rating of a fuel is a measure of its resistance to knock. The antiknock requirement of an engine depends on engine design and operation, as well as atmospheric conditions. Fuel with an antiknock rating higher than that required for knock-free operation does not improve performance.

X1.2.3 A decrease in antiknock rating may cause vehicle performance loss. However, vehicles equipped with knock limiters can show a performance improvement as the antiknock quality of the fuel is increased in the range between customer audible knock and knock-free operation. The loss of power and the damage to an automotive engine due to knocking are generally not significant until the knock intensity becomes very severe. Heavy and prolonged knocking may cause power loss and damage to the engine.

X1.3 Laboratory Octane Number

X1.3.1 The two recognized laboratory engine test methods for determining the antiknock rating of fuels are the Research method (Test Methods D 2699 or D 2885) and the Motor method (Test Methods D 2700 or D 2885). The following paragraphs define the two methods and describe their significance as applied to various equipment and operating conditions.

X1.3.2 Research octane number is determined by a method that measures fuel antiknock level in a single-cylinder engine under mild operating conditions; namely, at a moderate inlet mixture temperature and a low engine speed. Research octane number tends to indicate fuel antiknock performance in engines at wide-open throttle and low-to-medium engine speeds.

X1.3.3 Motor octane number is determined by a method that measures fuel antiknock level in a single-cylinder engine under more severe operating conditions than those employed in the Research method; namely, at a higher inlet mixture temperature and at a higher engine speed. It indicates fuel antiknock performance in engines operating at wide-open throttle and high engine speeds. Also, Motor octane number tends to indicate fuel antiknock performance under part-throttle, road-load conditions.

X1.4 Road Octane Number

X1.4.1 The road octane of a fuel is the measure of its ability to resist knock in customers' vehicles, and is ultimately of more importance than laboratory octane numbers. Since road octanes are difficult to measure and interpret, the industry has agreed to use ASTM laboratory engine tests to

estimate the road octane performance of spark-ignition engine fuel in vehicles.

X1.4.2 The antiknock index (AKI) is the arithmetic average of the Research octane number (RON) and Motor octane number (MON):

$$AKI = (RON + MON)/2 \quad (X1.1)$$

This value is called by a variety of names, in addition to antiknock index, including:

Octane rating
Posted octane
(R + M)/2 octane

X1.4.3 The AKI is posted on retail gasoline dispensing pumps in the United States and is referred to in car owners' manuals. The AKI is also required for certification at each wholesale fuel transfer and is referred to in United States federal law as "Octane Rating."⁹

X1.4.4 The most extensive data base that relates the laboratory engine test methods for Research and Motor octane to actual field performance of fuel in vehicles is the annual Coordinating Research Council (CRC)¹⁰ Octane Number Requirement Survey conducted for new light-duty vehicles. Analysis of these data shows that the antiknock performance of a fuel in some vehicles may correlate best with Research octane number, while in others, it may correlate best with Motor octane number. These correlations also differ from model year-to-model year or from vehicle population-to-vehicle population, reflecting changes in engine designs over the years.

X1.4.5 The antiknock index of a fuel approximates the CRC road octane ratings for many vehicles. However, the user must be guided also by experience as to which fuel is most appropriate for an individual vehicle. The antiknock index formula is reviewed periodically and may have to be adjusted in the future as engines and fuels continue to evolve. The present (RON + MON)/2 formula is an estimate and is not an absolute measure of fuel antiknock performance in general or in any specific vehicle.

X1.4.6 Car antiknock requirements vary, even within a single model, so the statistical distribution of the octane needs of any car population are usually shown in graphical form, as shown in Fig. X1.1. As antiknock index increases, larger and larger fractions of the car population in question will be free of knock, that is, be "satisfied" with the octane quality of fuels at or above that level of antiknock index. The data in Fig. X1.1 are for new model cars and trucks sold in the United States in the model year 1988 and are included as an example of the antiknock requirement distribution, not as a data reference.

X1.4.7 According to the winter 1988-1989 motor gasoline survey published by the National Institute for Petroleum and Energy Research, unleaded fuel antiknock indexes in current practice range from a low near 84 in the mountain areas to a high of near 94. Companies typically market two or three unleaded grades of fuel, one of which usually has a

⁹ Details of this regulation can be found in Code of Federal Regulations Title 16, Chapter 1, Subchapter C, part 306 (16 CFR 306), U.S. Government Printing Office, Superintendent of Documents, Washington DC 20402.

¹⁰ Coordinating Research Council, Inc., 219 Perimeter Center Parkway, Atlanta, GA 30346.

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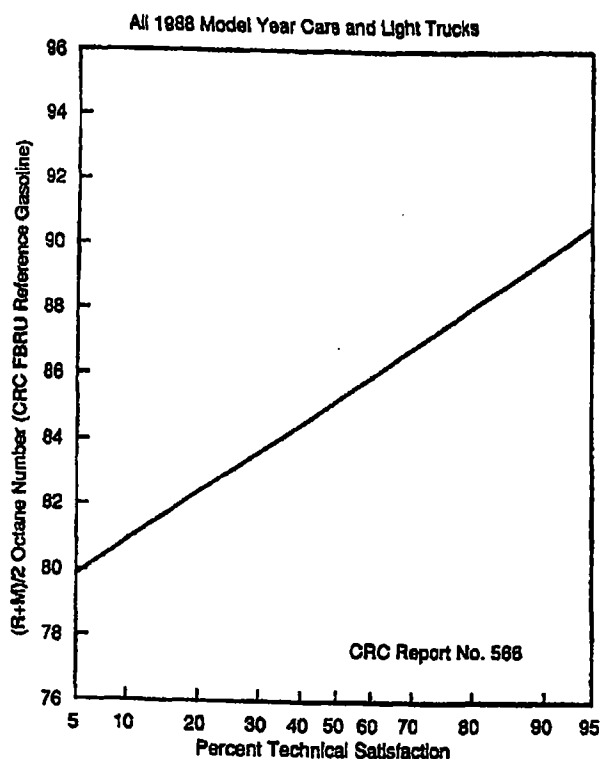


FIG. X1.1 An Example of the Statistical Distribution of Vehicle Antiknock Requirements

minimum antiknock index of 87, for which most post-1971 vehicles are designed. Most companies also market a higher octane fuel with an antiknock index of 91 or above. This fuel is intended to satisfy those vehicles with a higher octane requirement. Some companies offer three grades of unleaded fuel. The third grade usually has an antiknock index of 89. Leaded fuel is still available in some markets and usually has an antiknock index of 88 or 89.

X1.4.8 Marketers set the grades and octane based on their perception of the technical and competitive needs in the market.

X1.4.9 Antiknock indexes of fuel sold in current practice in the United States are shown in Table X1.1 for both unleaded and leaded fuels.

X1.5 Precision and Bias of Antiknock Index

X1.5.1 The following statements apply to the precision and bias of antiknock index of fuel, which is a composite quantity not addressed in any other standard.

X1.5.2 The precision of the antiknock index, $(RON + MON)/2$, is a function of the individual precisions of Research (Test Method D 2699) and Motor (Test Method D 2700) octane numbers. The repeatability and reproducibility variances for these test methods are summed and divided by four to obtain the variance of the antiknock index.

X1.5.2.1 *Repeatability*—The difference between two sets of antiknock index determinations, where two test results by

TABLE X1.1 Automotive Spark-Ignition Engine Fuel Antiknock Indexes in Current Practice

Unleaded Fuel ^A (for vehicles that can or must use unleaded fuel)	
Antiknock Index ^{B,C,D,E} (RON + MON)/2	Application
87	Designed to meet antiknock requirements of most 1971 and later model vehicles
89	Satisfies vehicles with somewhat higher antiknock requirements
91 and above	Satisfies vehicles with high antiknock requirements
Leaded Fuel (for vehicles that can or must use leaded fuel)	
Antiknock Index ^{B,C,D,E} (RON + MON)/2	Application
88	For most vehicles that were designed to operate on leaded fuel

^A Unleaded fuel having an antiknock index of at least 87 should also have a minimum Motor octane number of 82 in order to adequately protect those vehicles that are sensitive to Motor octane quality.

^B Reductions in vehicle antiknock requirements for altitude are shown in Fig. X1.2.

^C Reductions in vehicle antiknock requirements for seasonal variations are shown in Fig. X1.3.

^D Not all antiknock index levels listed in this table are available at all locations.

^E The Federal Trade Commission requires octane posting and certification in accordance with 16 CFR Part 306.

each octane number method were obtained by one operator, with the same apparatus under constant operating conditions on identical test material would, in the long run, and in the normal and correct operation of the test methods, exceed the values in the following table in only one case in twenty.

X1.5.2.2 *Reproducibility*—The difference between two independent sets of antiknock index determinations, obtained by different operators working in different laboratories on identical test material would, in the long run, and in the normal and correct operation of the test methods, exceed the values in the following table in only one case in twenty.

Antiknock Index	Repeatability Limits, Antiknock Index Units	Reproducibility Limits, Antiknock Index Units
83	0.2	0.7
85	0.2	0.7
87	0.2	0.7
89	0.2	0.6
91	0.2	0.6
93	0.2	0.6
95	—	0.6
97	—	0.7

NOTE X1.1—These precision limits were calculated from Research and Motor octane number results obtained by member laboratories of the ASTM National Exchange Group (NEG) participating in a cooperative testing program. The data obtained during the period 1980 through 1982 have been analyzed in accordance with RR:D02-1007, "Manual on Determining Precision Data for ASTM Methods on Petroleum Products and Lubricants," Spring, 1973.

X1.5.2.3 *Bias*—Since knock ratings are determined by the conditions of the empirical test methods involved, bias cannot be determined.

X1.6 Effects of Altitude and Weather on Vehicle Antiknock Requirement

X1.6.1 A vehicle's antiknock requirement can vary with changes in altitude, ambient temperature, and humidity, depending on the control system of the vehicle. New vehicles have sensors to measure, and engine management computers

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which take into account, such conditions as air charge temperature and barometric pressure. These vehicles are designed to have the same antiknock requirement at all altitudes and a reduced sensitivity to changes in ambient temperature. This more sophisticated control technology began to be used extensively in 1984. This technology, while constantly evolving and improving, is used on almost all new vehicles. This means that many vehicles in today's fleet require fuel having the same antiknock index regardless of changes in altitude or ambient temperatures. Older vehicles which do not have sophisticated control systems will likely experience changes in antiknock requirement due to changes in altitude and weather conditions. However, the changes in antiknock requirement indicated in the following sections apply to a continually smaller part of the vehicle fleet.

X1.6.2 The antiknock requirement of an older vehicle decreases as altitude increases, primarily due to reduction in mixture density caused by reduced atmospheric pressure. The change in antiknock requirement for altitude for older vehicles is given in Fig. X1.2. Boundaries of the areas defined and the corresponding antiknock index reductions were established to protect vehicles driven from a higher altitude to a lower altitude (and, hence higher antiknock requirement) area while using a fuel obtained in the high altitude area.

X1.6.3 Tests by CRC and other organizations have shown that the decrease in antiknock requirements with altitude is larger for most models between 1971 and 1984, designed to

use a fuel with an antiknock index of 87, than for pre-1971 vehicles. Generally the pre-1971 vehicles have high compression ratios and were designed for fuels with an antiknock index of 88 or higher. Fuels with antiknock indexes below 89 are adjusted by a larger factor than those with an antiknock index of 89 or greater.

X1.6.4 The antiknock requirements of older vehicles rise with increasing ambient temperature on the average by 0.097 MON per degree Celsius (0.054 MON per degree Fahrenheit).

X1.6.5 The antiknock requirements of both older and new vehicles decrease with increasing specific humidity by 0.245 MON per gram of water per kilogram of dry air (0.035 MON per grain of water per pound of dry air).

X1.6.6 Because temperature and humidity of geographical areas are predictable throughout the year from past weather records, antiknock index levels can be adjusted to match seasonal changes in vehicle antiknock requirements. Fig. X1.3 defines the boundaries of areas and the typical reduction in vehicle antiknock requirements for weather for older vehicles. This figure may not apply to newer vehicles.

X1.7 Leaded Versus Unleaded Fuel Needs

X1.7.1 In addition to selecting the appropriate antiknock index to meet vehicle antiknock needs, a choice must be made between leaded and unleaded fuel. Vehicles that must use unleaded fuel are required by Environmental Protection Agency regulation to have permanent labels on the instrument panel and adjacent to the fuel tank filler inlet reading "Unleaded Fuel Only." Most 1975 and later model passenger cars and light trucks are in this category. Most 1971-1974 vehicles can use leaded or unleaded fuel. Pre-1971 vehicles were designed for leaded fuel; however, unleaded fuel of suitable antiknock index may generally be used in these vehicles, except that leaded fuel should be used periodically (after a few tankfuls of unleaded fuel have been used). Leaded fuel may be required in some vehicles, particularly trucks, in heavy-duty service and some farm equipment. Instructions on fuel selection are normally provided in publications of vehicles manufacturers (for example, owner's manuals, service bulletins, etc.). Antiknock agents other than lead alkyls may be used to increase the antiknock index of fuels, and their concentrations may also be limited due to either performance or legal requirements.

X1.8 Volatility

X1.8.1 In most spark-ignition internal combustion engines, the fuel is metered in liquid form through the carburetor or fuel injector, and is mixed with air and partially vaporized before entering the cylinders of the engine. Consequently, volatility is an extremely important characteristic of motor fuel.

X1.8.2 At high operating temperatures, fuels can boil in fuel pumps, lines, or carburetors. If too much vapor is formed, the fuel flow to the engine can be decreased, resulting in loss of power, rough engine operation, or engine stoppage. These conditions are known as "vapor lock." Conversely, fuels that do not vaporize sufficiently can cause hard starting of cold engines and poor warm-up performance. These conditions can be minimized by proper selection of volatility requirements, but cannot always be

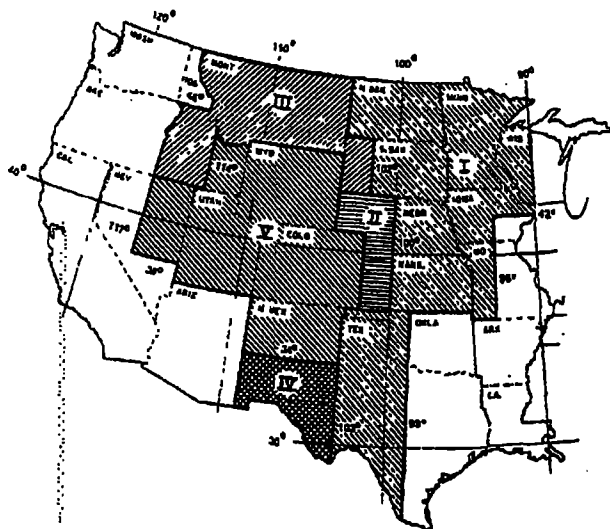


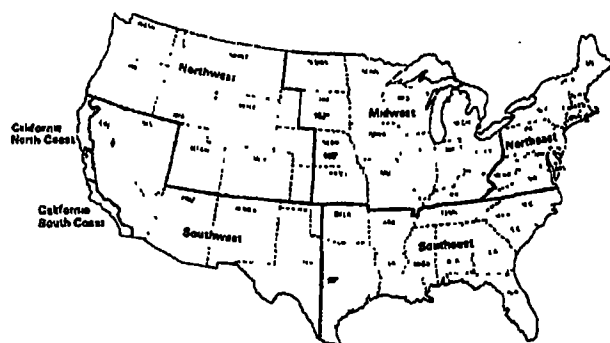
FIG. X1.2 Reduction in Vehicle Antiknock Requirements for Altitude^{A,B}

Area	Less than 89 AKI	89 AKI or Greater
I	0.7	0.5
II	1.5	1.5
III	2.2	1.5
IV	3.0	2.0
V	4.5	3.0

^A Fuel may be marketed using these reductions, but actual antiknock index minimums must be posted.

^B While the reductions in this table apply to most pre-1984 vehicles, the control technology on almost all new vehicles will cause them to have no reduction in antiknock requirement at higher altitudes.

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FIG. X1.3 Reduction in Vehicle Antiknock Requirements for Weather^a

	J	F	M	A	M	J	J	A	S	O	N	D
Northeast	1.0	0.5	0.5	0	0	0	0	0	0	0.5	0.5	1.0
Southeast	0.5	0	0	0	0	0.5	0.5	0.5	0.5	0	0	0.5
Midwest	1.0	0.5	0.5	0	0	0	0	0	0	0	0.5	1.0
Northwest	1.0	1.0	0.5	0.5	0	0	0	0	0	0.5	1.0	1.0
Southwest	1.0	0.5	0	0	0	0	0	0	0	0	0.5	1.0
California ^a												
No Coast	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0	0	0.5	0.5
So Coast	0	0	0.5	0.5	1.0	1.0	1.0	0.5	0.5	0	0	0
Alaska	1.0	1.0	0.5	0.5	0	0	0	0	0	0.5	1.0	1.0
Hawaii	0	0	0	0	0	0	0	0	0	0	0	0

^a Fuel may be marketed using these reductions, but actual antiknock index minimums must be posted.

^a Details of California coastal areas are shown in Footnote C of Table 4.

avoided. For example, during spring and fall a fuel of volatility suitable for satisfactory starting at low ambient temperatures can cause problems in some engines under higher ambient temperature operating conditions.

X1.8.3 Six vapor pressure/distillation classes and five vapor lock protection (vapor-liquid ratio) classes of fuel are provided to satisfy vehicle performance requirements under different climatic conditions and to comply with U.S. EPA vapor pressure limits for the control period of May 1 through September 15. Class A and Class AA specify the EPA maximum vapor pressure limits of 9.0 psi and 7.8 psi, respectively. Volatility of fuel is specified by an alphanumeric designation. The letter specifies the vapor pressure/distillation class and the number specifies the vapor lock protection class. The vapor pressure/distillation classes are needed to comply with the EPA vapor pressure regulations and are not based on vehicle performance during the EPA control period. The separate vapor lock protection classes are provided because under most ambient conditions the EPA regulations specify a lower vapor pressure than would be required to prevent hot fuel handling problems. If the corresponding and unnecessarily more restrictive vapor-liquid ratios were specified when the EPA regulations are in effect, it could result in reduced fuel production, manufacturing hardships, and increased fuel costs. The schedule for seasonal and geographical distribution indicates the appropriate alphanumeric volatility requirement or requirements for each month in all areas of the United States, based on altitude and expected air temperatures, and on EPA vapor pressure regulations. Volatility limits are established in terms of vapor-liquid ratio, vapor pressure, and distillation properties.

X1.8.4 For sea-level areas outside of the United States

where vapor pressure requirements are not as restrictive as those specified by EPA, the following ambient temperatures are for guidance in selecting the appropriate alphanumeric designation:

Alphanumeric Volatility Designation	10th Percentile 6-h Minimum Daily Temperature, °C (°F)	90th Percentile Maximum Daily Temperature, °C (°F)
A-1	>16 (60)	≥43 (110)
B-2	>10 (50)	<43 (110)
C-3	>4 (40)	<36 (97)
D-4	>-7 (20)	<29 (85)
E-5	≤-7 (20)	<21 (69)

The 6-h minimum temperature is the highest temperature of the six coldest consecutive hourly temperature readings of a 24-h day. The 6-h minimum temperature provides information on the cold-soak temperature experienced by a vehicle. The 10th percentile of this temperature statistic indicates a 10 % expectation that the 6-h minimum temperature will be below this value during a month. The 90th percentile maximum temperature is the highest temperature expected during 90 % of the days, and provides information relative to peak vehicle operating temperatures during warm and hot weather. For areas above sea level, the 10th percentile 6-h minimum temperature should be increased by 3.6°C/1000 m (2°F/1000 ft) of altitude, and the 90th percentile maximum should be increased by 4.4°C/1000 m (2.4°F/1000 ft) of altitude before comparing them to the sea level temperature. These corrections compensate for changes in fuel volatility caused by changes in barometric pressure due to altitude.

X1.9 Vapor Pressure

X1.9.1 The vapor pressure of fuel must be sufficiently high to ensure ease of engine starting, but it must not be so high as to contribute to vapor lock or excessive evaporative emissions and running losses.

X1.9.2 Test Methods D 4953, D 5190, D 5191, or D 5482 provide procedures for determining the vapor pressures of gasoline or gasoline-oxygenate blends.

X1.10 Vapor-Liquid Ratio

X1.10.1 Vapor-liquid ratio (V/L) is the ratio of the volume of vapor formed at atmospheric pressure to the volume of fuel tested in Test Method D 2533. The V/L increases with temperature for a given fuel. Because some oxygenates are miscible with the glycerin confining fluid, Test Method D 2533 has been modified so mercury can also be used as a confining fluid. Either procedure may be used for determining V/L of gasoline. The mercury confining fluid shall be used for gasoline-oxygenate blends. Test Method D 5188 is an evacuated chamber method for determining temperatures for vapor-liquid ratios between 8 to 1 and 75 to 1. Test Method D 5188 is applicable to both gasoline and gasoline-oxygenate blends.

X1.10.2 The temperature of the fuel system and the V/L that can be tolerated without vapor lock vary from vehicle to vehicle and with operating conditions. The tendency of a fuel to cause vapor lock, as evidenced by loss of power during full-throttle accelerations, is indicated by the gasoline temperature at a V/L of approximately 20. A similar relationship for gasoline-oxygenate blends has also been determined. The temperature at which the maximum V/L is specified for

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each gasoline volatility class is based on the ambient temperatures and the altitude associated with the use of the class.

X1.11 Vapor-Liquid Ratio (Estimated)

X1.11.1 Three techniques for estimating temperature- V/L values using vapor pressure (Test Methods D 4953, D 5190, D 5191, or D 5482) and distillation (Test Method D 86) results are given in Appendix X2; they apply to gasoline only.

X1.12 Distillation

X1.12.1 Test Method D 86 for distillation provides another measure of the volatility of fuels. Table 1 designates the limits for end-point temperature and the temperatures at which 10 %, 50 %, and 90 % by volume of the fuel is evaporated. These distillation characteristics, along with vapor pressure and V/L characteristics, affect the following vehicle performance characteristics: starting, driveability, vapor lock, dilution of the engine oil, fuel economy, and carburetor icing.

X1.12.2 The 10 % evaporated temperature of fuel should be low enough to ensure starting under normal temperatures.

X1.12.3 Fuels having the same 10 % and 90 % evaporated temperatures can vary considerably in driveability performance because of differences in the boiling temperatures of the intermediate components, or fractions. Driveability and idling quality are affected by the 50 % evaporated temperature. The 90 % evaporated and end-point temperatures should be low enough to minimize dilution of the engine oil.

X1.13 Corrosion

X1.13.1 Fuels must pass the copper strip corrosion test to minimize corrosion in fuel systems due to sulfur compounds in the fuel. Some fuels corrode fuel system metals other than copper, but there are no ASTM test methods to evaluate corrosion of these metals. Depending on the type and concentration of oxygenate, gasoline-oxygenate blends can corrode metals such as zinc, magnesium, aluminum, steel, and tin. However, at this time there is no test method with a known correlation to field performance. Consequently, additional corrosion tests are needed.

X1.14 Solvent-Washed Gum Content

X1.14.1 The test for solvent-washed gum content measures the amount of residue after evaporation of the fuel and following a heptane wash. The heptane wash removes the heptane-soluble, non-volatile material such as additives, carrier oils used with additives, and heavier hydrocarbons such as diesel fuels, etc. Solvent-washed gum consists of fuel-insoluble gum and fuel-soluble gum. The fuel-insoluble portion can clog fuel filters. Both can be deposited on surfaces when the fuel evaporates.

X1.14.2 Solvent-washed gum can contribute to deposits on the surfaces of carburetors, fuel injectors, and intake manifolds, ports, valves, and valve guides. The impact of solvent-washed gum on malfunctions of modern engines is not well established and the current specification limit is historic rather than the result of recent correlative studies. It depends on where the deposits form, the presence of other deposit precursors such as airborne debris, blowby and

exhaust gas recirculation gases, and oxidized engine oil, and the amount of deposits.

X1.14.3 The difference between the unwashed and solvent-washed gum content values can be used to assess the presence and amount of nonvolatile material in the fuel. Additional analytical testing is required to determine if the material is additive, carrier oil, diesel fuel, etc.

X1.15 Sulfur

X1.15.1 The limit on sulfur content is included to protect against engine wear, deterioration of engine oil, and corrosion of exhaust system parts.

X1.16 Oxidation Stability

X1.16.1 The induction period as measured in the oxidation stability test is used as an indication of the resistance of fuel to gum formation in storage. Experience indicates that fuels with an induction period equal to or greater than that in Table 3 generally have acceptable short-term storage stability. However, correlation of the induction period with the formation of gum in storage can vary markedly under different storage conditions and with different fuels.

X1.17 Water Tolerance

X1.17.1 Water tolerance is the ability of a fuel to dissolve water without phase separation. It is not of concern for gasoline because of the very low solubility of water in hydrocarbons. Water tolerance is of some concern with gasoline-ether blends because of the limited solubility of ethers in water, but it is of great concern for gasoline-alcohol blends because of the very high solubility of alcohols in water. If the amount of water exceeds the water tolerance limit of the blend, the fuel will separate into a lower alcohol-rich aqueous phase and an upper alcohol-lean hydrocarbon phase. The resultant aqueous phase is not suitable as an automotive fuel and may be corrosive to many metals. Similarly, the hydrocarbon portion may also not be suitable as a fuel since removal of the alcohol component will change the volatility and antiknock characteristics.

X1.17.2 The most important factor, besides the quantity of water contacted, which governs the water tolerance of a fuel is its temperature. As the temperature of the blend decreases, water tolerance decreases. The test method found in Annex A1 is intended to determine the ability of gasoline-oxygenate blends to retain water in solution or in a stable suspension at the lowest temperature to which they are likely to be exposed in use. Some other factors that affect water tolerance are concentration and type of oxygenate and aromatics content of the fuel.

X1.17.3 With some gasoline-oxygenate blends, formation of a haze may occur when filling a storage tank that contains water bottoms, while commingling of gasoline-oxygenate blends with gasoline, or when a sufficient decrease in temperature occurs. However, the haze may not be stable and the fuel will clear usually in a short period of time.

X1.17.4 A more critical water tolerance concern is the potential increase in storage tank water bottoms. This can occur when some gasoline-oxygenate blends and gasoline-alcohol blends in particular are added to a tank that contains sufficient water to extract some or all of the oxygenate component from the fuel.

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X2. ESTIMATING TEMPERATURE-V/L VALUES FOR GASOLINE

X2.1 Scope

X2.1.1 Three techniques are presented here for estimating temperature-V/L data from vapor pressure and distillation test results¹¹ on gasolines only. They are provided for use as a guideline when V/L data measured by Test Method D 2533 are not available. One method is designed for computer processing, one is a simpler linear technique, while the other is a nomogram form of this linear equation.

X2.1.2 These techniques are not optional procedures for measuring V/L. They are supplementary tools for estimating temperature-V/L relationships with reasonable accuracy when used with due regard for their limitations.

X2.1.3 Test Method D 2533 is the referee V/L procedure and shall be used when calculated values are questionable.

X2.1.4 These techniques are not intended for, nor are they necessarily applicable to, fuels of extreme distillation or chemical characteristics such as would be outside the range of normal commercial motor gasolines. Thus, they are not applicable in all instances to gasoline blending stocks or specially blended fuels.

X2.2 Computer Method

X2.2.1 **Summary**—The values of four intermediate functions, A , B , C , and D , are derived from the gasoline vapor pressure and distillation temperatures at 10, 20, and 50 % evaporated. Values for A , B , C , and D can be obtained either from equations or from a set of charts. Sections X2.2.2.1 through X2.2.2.3 provide A , B , C , and D values using SI units; X2.2.2.6 through X2.2.2.8 provide A , B , C , and D values using inch-pound units. Estimated temperatures at a V/L of 4, 10, 20, 30, and 45 are then calculated from A , B , C , and D . Estimated temperatures at an intermediate V/L can be obtained by interpolation.

X2.2.2 Procedure:

X2.2.2.1 Establish input data from vapor pressure (Test Methods D 4953, D 5190, D 5191, or D 5482) and distillation (Test Method D 86) test results as follows:

E = distillation temperature, °C at 10 % evaporated,

F = distillation temperature, °C at 20 % evaporated,

G = distillation temperature, °C at 50 % evaporated,

$H = G - E$, °C, (X2.1)

P = vapor pressure, kPa,

$Q = F - E$, °C, and (X2.2)

$R = H/Q$, except that if H/Q is greater than 6.7, make $R = 6.7$. (X2.3)

X2.2.2.2 If A , B , C , and D , are to be calculated use the following equations:

$$A = 102.859 - 1.36599P + 0.009617 P^2 - 0.000028281P^3 + 207.0097/P \quad (X2.4)$$

$$B = -5.36868 + 0.910540Q - 0.040187 Q^2 + 0.00057774Q^3 + 0.254183/Q \quad (X2.5)$$

$$S = -0.00525449 - 0.3671362/(P - 9.65) - 0.812419/(P - 9.65)^2 + 0.0009677R - 0.0000195828R^2 - 3.3502318R/P^2 + 1241.1531R/P^4 - 0.06630129R^2/P + 0.00627839R^3/P + 0.0969193R^2/P^2 \quad (X2.6)$$

$$C = 0.34205P + 0.55556/S \quad (X2.7)$$

$$D = 0.62478 - 0.68964R + 0.132708R^2 - 0.0070417R^3 + 5.8485/R \quad (X2.8)$$

X2.2.2.3 If A , B , C , and D , are to be obtained from charts, read them from Figs. X2.1, X2.2, X2.3, and X2.4, respectively.

X2.2.2.4 Calculate the estimated temperature (°C or °F) at V/L ratios 4, 10, 20, 30, and 45 from the following equations:

$$T_4 = A + B \quad (X2.9)$$

$$T_{45} = F + 0.125H + C \quad (X2.10)$$

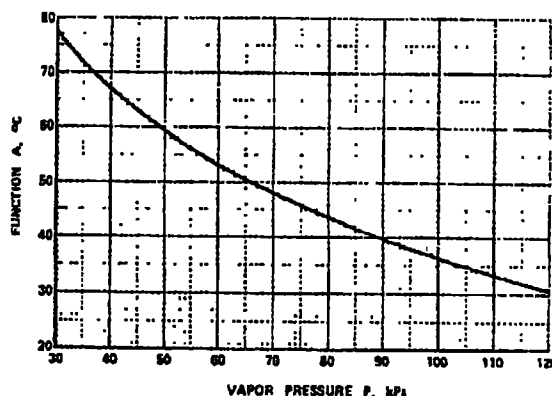


FIG. X2.1 Function A versus Vapor Pressure P

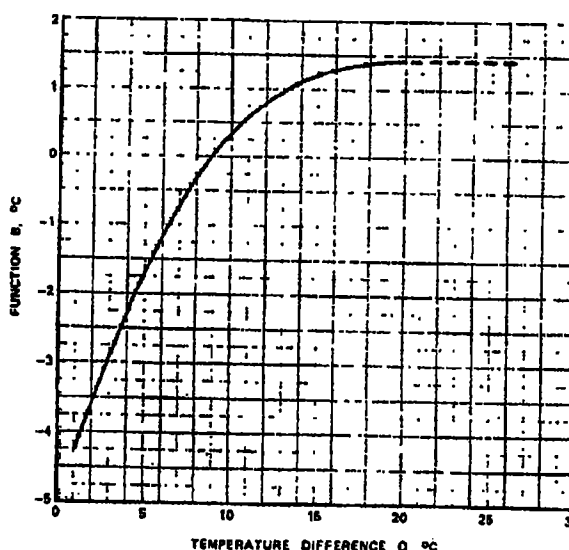


FIG. X2.2 Function B versus Distillation Temperature Difference Q

¹¹ A correlation of temperature-V/L ratio data with vapor pressure and distillation data was developed in 1943 and restudied in 1963 by panels of the Coordinating Research Council, Inc. See "Correlation of Gasoline Vapor Forming Characteristics with Inspection Test Data," *CRC Report No. 159*, Jan. 28, 1943 (or SAE Transaction, Vol. 52, August 1944, pp. 364-367) and "Study of CRC Calculated Temperature-V/L Technique," *CRC Report No. 370*, February 1963. The CRC correlation was modified by a task group of Subcommittee A of Committee D-2 to adapt it for computer processing, as well as the linear equation and the nomogram.

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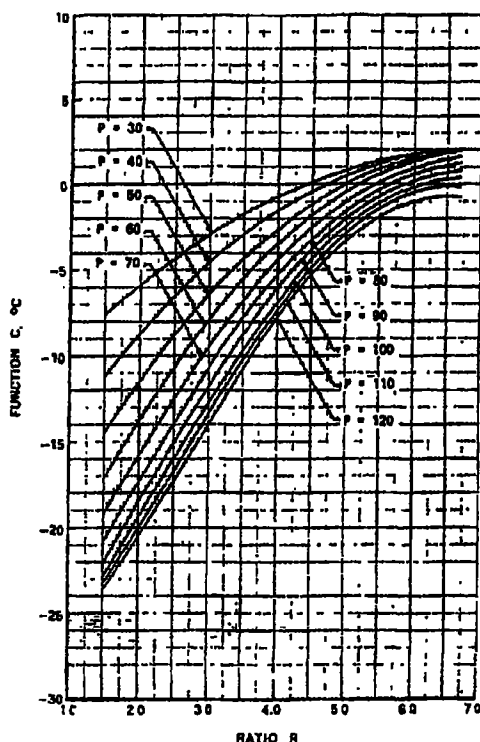


FIG. X2.3 Function C versus Ratio R and Vapor Pressure P

$$T_{10} = T_4 + 0.146341 (T_{45} - T_4) + D \quad (X2.11)$$

$$T_{20} = T_4 + 0.390244 (T_{45} - T_4) + 1.46519D \quad (X2.12)$$

$$T_{30} = T_4 + 0.634146 (T_{45} - T_4) + D \quad (X2.13)$$

where:

T_4 , T_{10} , T_{20} , T_{30} , and T_{45} are estimated temperatures at V/L ratios, 4, 10, 20, 30, and 45.

X2.2.2.5 If the temperature at an intermediate V/L ratio is to be estimated, either plot the values calculated in X2.2.2.4 and read the desired value from a smooth curve through the points, or use the Lagrange interpolation formula as follows:

$$TX = T_4 \left(\frac{X-10}{4-10} \times \frac{X-30}{4-30} \times \frac{X-45}{4-45} \right) + T_{10} \left(\frac{X-4}{10-4} \times \frac{X-30}{10-30} \times \frac{X-45}{10-45} \right) + T_{30} \left(\frac{X-4}{30-4} \times \frac{X-10}{30-10} \times \frac{X-45}{30-45} \right) + T_{45} \left(\frac{X-4}{45-4} \times \frac{X-10}{45-10} \times \frac{X-30}{45-30} \right) \quad (X2.14)$$

where:

X = the desired V/L ratio between 4 and 45, and
 TX = the estimated temperature at V/L ratio X .

X2.2.2.6 If inch-pound units are used, establish input data from vapor pressure (Test Methods D 4953, D 5190, D 5191, or D 5482) and distillation (Test Method D 86) test results as follows:

E = distillation temperature, °F, at 10 % evaporated,

F = distillation temperature, °F, at 20 % evaporated,

G = distillation temperature, °F, at 50 % evaporated,

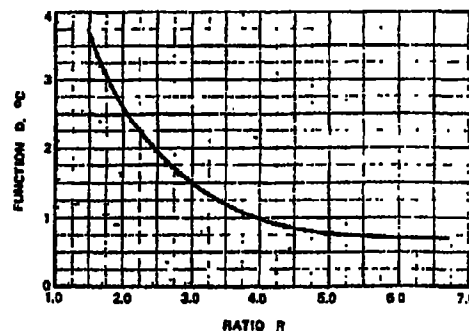


FIG. X2.4 Function D versus Ratio R

$$H = G - E, \text{ °F} \quad (X2.15)$$

P = vapor pressure, psi,

$$Q = F - E, \text{ °F, and} \quad (X2.16)$$

$$R = H/Q, \text{ except that if } H/Q \text{ is greater than 6.7, make } R = 6.7. \quad (X2.17)$$

X2.2.2.7 If A , B , C , and D are to be calculated in inch-pound units, use the following equations:

$$A = 217.147 - 16.9527P + 0.822909P^2 - 0.0166849P^3 + 54.0436/P \quad (X2.18)$$

$$B = -9.66363 + 0.910540Q - 0.0223260Q^2 + 0.000178314Q^3 + 0.823553/Q \quad (X2.19)$$

$$S = -0.00525449 - 0.0532486/(P - 1.4) - 0.0170900/(P - 1.4)^2 + 0.0009677R - 0.0000195828R^2 - 0.0704753R/P^2 + 0.549224R/P^4 - 0.00961619R^2/P + 0.000910603R^3/P + 0.00203879R^2/P^2 \quad (X2.20)$$

$$C = 4.245P + 1.0/S \quad (X2.21)$$

$$D = 1.12460 - 1.24135R + 0.238875R^2 - 0.0126750R^3 + 10.5273/R \quad (X2.22)$$

X2.2.2.8 If A , B , C , and D are to be obtained from charts in inch-pound units, read them from Figs. X2.5, X2.6, X2.7, and X2.8, respectively.

X2.2.2.9 Calculate the estimated temperatures, °F, at V/L

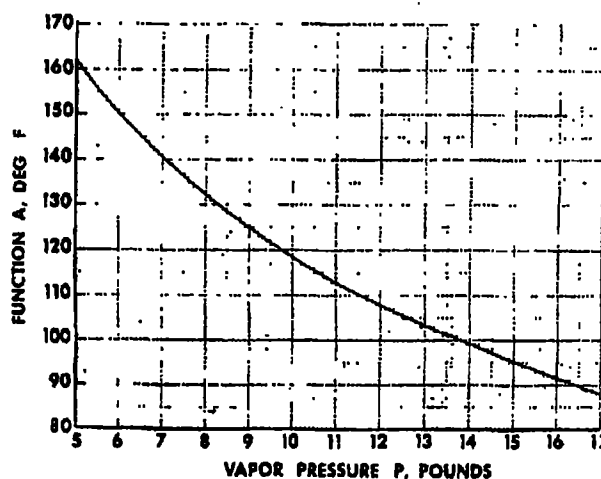


FIG. X2.5 Function A versus Vapor Pressure P

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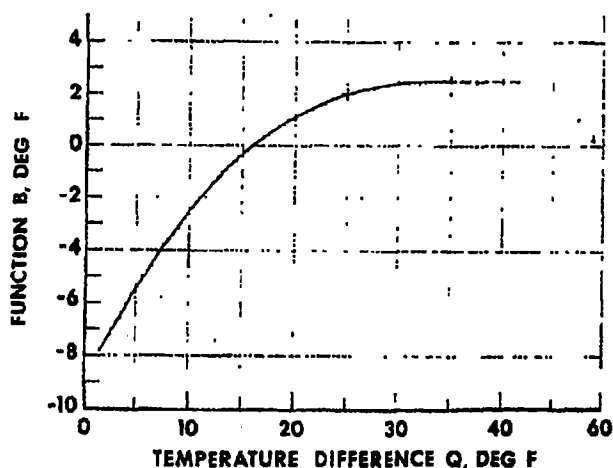


FIG. X2.6 Function B versus Distillation Temperature Difference Q

ratios 4, 10, 20, 30, and 45 using the equations in X2.2.2.4 and X2.2.2.5.

X2.3 Linear Equation Method

X2.3.1 Summary—As given, these two equations provide only the temperatures (°C or °F) at which a V/L value of 20 exists. They make use of two points from the distillation curve, T_{10} and T_{50} (°C or °F), and the vapor pressure (kPa or psi) of the gasoline with constant weighting factors being applied to each. Experience has shown that data obtained with these simple linear equations generally are in close agreement with those obtained by the computerized version given above. The limitations pointed out in X2.1.1 through X2.1.4 must be kept in mind when use is made of this procedure.

X2.3.2 Procedure—Obtain 10 % evaporated and 50 %

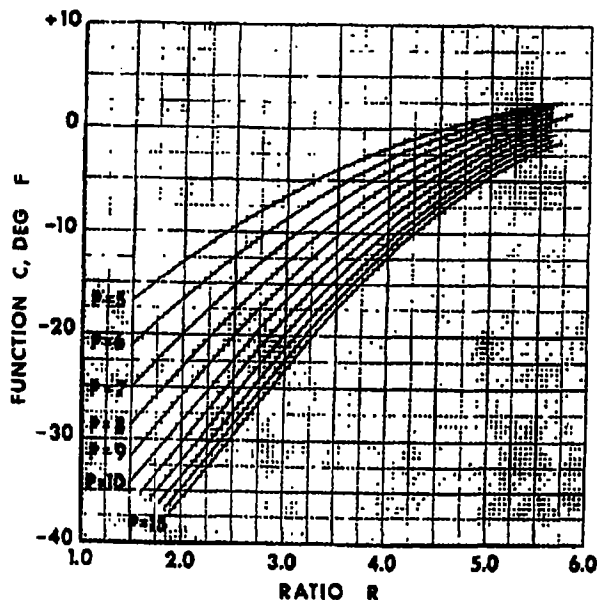


FIG. X2.7 Function C versus Ratio R and Vapor Pressure P

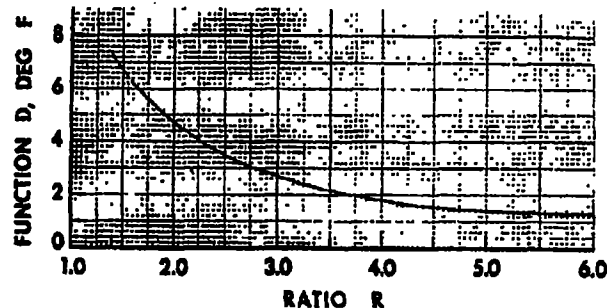


FIG. X2.8 Function D versus Ratio R

evaporated points from the distillation curve (Test Method D 86) along with the vapor pressure value (Test Methods D 4953, D 5190, D 5191, or D 5482); apply these directly in the equation.

$$T_{V/L=20} = 52.47 - 0.33 (VP) + 0.20 T_{10} + 0.17 T_{50} \quad (X2.23)$$

where:

$T_{V/L=20}$ = temperature, °C, at V/L of 20:1,

VP = vapor pressure, kPa,

T_{10} = distillation temperature, °C, at 10 % evaporated, and

T_{50} = distillation temperature, °C, at 50 % evaporated.

or in the inch-pound customary unit equation:

$$T_{V/L=20} = 114.6 - 4.1 (VP) + 0.20 T_{10} + 0.17 T_{50} \quad (X2.24)$$

where:

$T_{V/L=20}$ = temperature, °F, at V/L of 20:1,

VP = vapor pressure, psi,

T_{10} = distillation temperature, °F, at 10 % evaporated, and

T_{50} = distillation temperature, °F, at 50 % evaporated.

X2.4 Nomogram Method

X2.4.1 Summary—Two nomograms have been developed and are included herein (Figs. X2.9 and X2.10) to provide the same function as the linear equations procedure outlined above. Figure X2.9 is in SI units and Fig. X2.10 is in inch-pound units. The nomograms are based on the two equations and the same limitations apply to their use in estimating V/L (20) temperatures.

X2.4.2 Procedure—Obtain 10 % evaporated and 50 % evaporated points from the distillation curve (Test Method D 86) along with the vapor pressure value (Test Methods D 4953, D 5190, D 5191, or D 5482). Select the SI unit (Fig. X2.9) or inch-pound unit (Fig. X2.10) nomogram based on the units of T_{10} , T_{50} , and VP. Using a straightedge, locate the intercept on the line between the " T_{10} and T_{50} " scales after selecting the applicable T_{10} and T_{50} values. From this intercept and the proper point on the "VP" scale, a second intercept can be obtained on the " $T_{V/L=20}$ " scale to provide the desired value directly.

X2.5 Precision

X2.5.1 The precision of agreement between temperature- V/L data estimated by any one of these three techniques and data obtained by Test Method D 2533 has not been established.

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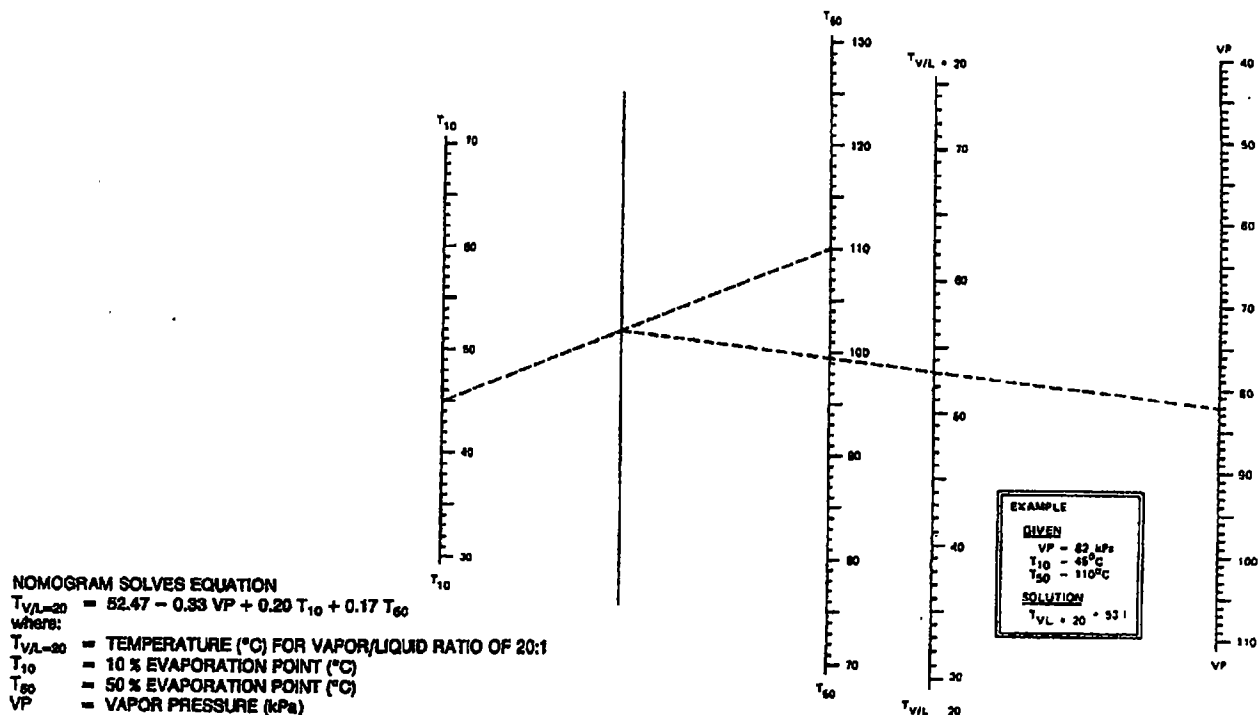


FIG. X2.9 Relationship Between Gasoline Volatility and Temperature for V/L Ratio at Sea Level—SI Units

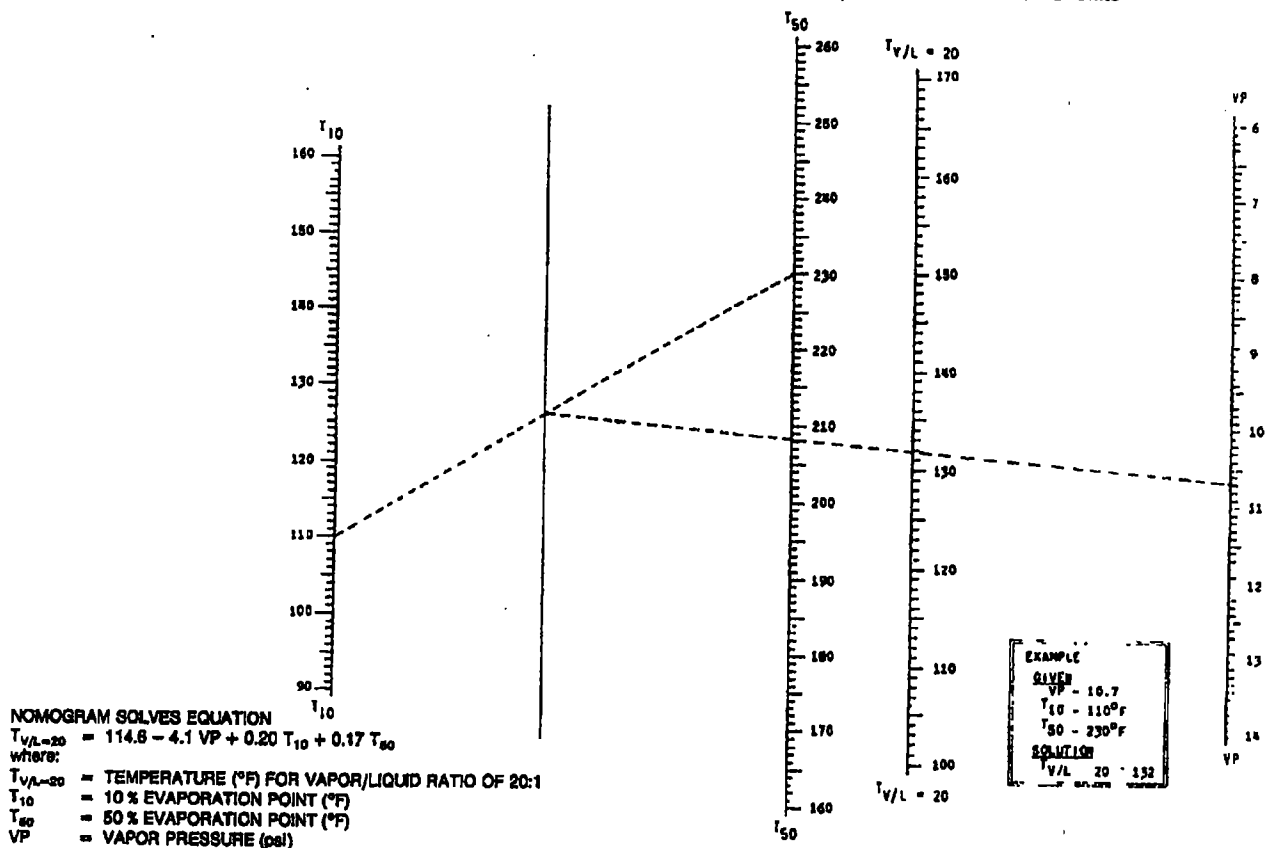


FIG. X2.10 Relationship Between Gasoline Volatility and Temperature for V/L Ratio of 20 at Sea Level—Inch-Pound Units



X3. SUMMARY OF EPA REGULATIONS APPLICABLE TO SPARK-IGNITION ENGINE FUEL

X3.1 EPA Applicable Vapor Pressure Standards

X3.1.1 Under authority of the Clean Air Act, the U.S. Environmental Protection Agency (EPA) issued, effective May 1992, vapor pressure control standards for leaded and unleaded gasoline and leaded and unleaded gasoline-oxygenate blends. Some states, notably California, have more restrictive vapor pressure limits.

X3.1.2 Details of the EPA regulations and test methods are available in Part 80 of Title 40 of the Code of Federal Regulations (40 CFR Part 80). For specific state vapor pressure regulations, the state of interest should be contacted.

X3.1.3 The EPA maximum vapor pressure limits of 7.8 psi and 9.0 psi are shown in Table 1 as Classes AA and A, respectively. The EPA requirements for each distribution area are shown in Table 4 for the period May 1 through September 15. For the month of May, the EPA limits only apply to finished gasoline and gasoline-oxygenate blend tankage at refineries, importers, pipelines, and terminals. For the period June 1 through September 15, the EPA limits apply to all locations of the distribution system. Footnotes D through F of Table 4 indicate the ozone nonattainment areas which are limited to 7.8 psi maximum and the appropriate vapor lock protection class. California has controls that vary for the different air basins from as early as March 1 at refineries through as late as October 31. There are no EPA vapor pressure limits for the states of Alaska or Hawaii.

X3.1.4 EPA regulations allow 1.0 psi higher values for gasoline-ethanol blends than the EPA limits shown in Tables 1 and 4 for the period May 1 through September 15. To qualify, the gasoline-ethanol blends must contain 9 to 10 volume % ethanol. Higher vapor pressure limits for gasoline-ethanol blends under state regulations vary for other time periods, and specific states of interest should be contacted to determine if higher limits apply.

X3.2 EPA Lead and Phosphorus Regulations

X3.2.1 *Unleaded Fuel*—The intentional addition of lead or phosphorus compounds to unleaded fuel is not permitted by EPA. EPA regulations limit their maximum concentrations to 0.05 g lead per U.S. gallon (0.013 g/L) and 0.005 g of phosphorus per U.S. gallon (0.0013 g/L) (see Test Method D 3231), respectively.

X3.2.2 *Leaded Fuel*—EPA regulations limit the lead concentration in leaded fuel to no more than 0.10 g per U.S. gallon (0.026 g/L) averaged per calendar quarter for each refinery. There is no EPA lead limit for any individual gallon of leaded fuel.

X3.3 EPA Oxygenate Regulations Applicable to Unleaded Gasoline-Oxygenate Blends

X3.3.1 *Substantially Similar Rule*:

X3.3.1.1 Section 211(f) (1) of the Clean Air Act prohibits introducing into commerce or increasing the concentration in use of, any fuel or fuel additive, which is not substantially similar to any fuel or fuel additive utilized for emissions certification of any model year 1975, or subsequent model year vehicle or engine, unless a waiver is obtained from the EPA.

X3.3.1.2 Gasoline-oxygenate blends are considered "sub-

stantially similar" if the following criteria are met.

(1) The fuel must contain carbon, hydrogen, and oxygen, nitrogen, or sulfur, or combination thereof, exclusively, in the form of some combination of the following:

- (a) Hydrocarbons;
- (b) Aliphatic ethers;
- (c) Aliphatic alcohols other than methanol;
- (d) (i) Up to 0.3 volume % methanol;

(ii) Up to 2.75 volume % methanol with an equal volume of butanol, or higher molecular weight alcohol;

(2) The fuel must contain no more than 2.0 mass % oxygen except fuels containing aliphatic ethers and/or alcohols (excluding methanol) must contain no more than 2.7 mass % oxygen.

(3) The fuel must possess, at the time of manufacture, all of the physical and chemical characteristics of an unleaded gasoline as specified by Specification D 4814 - 88 for at least one of the Seasonal and Geographical Volatility Classes specified in the standard.

Note X3.1—Opinion varies as to whether the EPA "substantially similar" rule requires unleaded gasolines that do not contain oxygenates to meet ASTM specifications.

X3.3.2 *Waivers*:

X3.3.2.1 EPA has issued waivers for blends of gasoline and ethanol (gasohol), gasoline and ethanol with cosolvents, and gasoline and methanol with cosolvents that are less limiting than the "substantially similar" rule. For the latest listing of waivers, EPA should be contacted.

X3.3.2.2 Gasoline-ethanol blends are not required by EPA to meet Specification D 4814 volatility limits (see X3.1.4 for vapor pressure limits). EPA has specified in all other waivers that the volatility of the finished gasoline-oxygenate blend must comply with Specification D 439 or D 4814 climatic and geographical limits.

X3.4 EPA Reformulated Gasoline (RFG)

X3.4.1 Reformulated gasoline (RFG) is a spark-ignition engine fuel formulated to reduce motor vehicle emissions of toxic and tropospheric ozone-forming compounds. The Clean Air Act Amendments of 1990 require that RFG be sold in nine metropolitan areas with the worst summertime ozone levels. Other areas that do not meet ambient ozone standards may petition EPA to require RFG. The various RFG regulations have been established by the EPA. EPA has also placed limits on conventional gasoline sold in the rest of the U.S. to prevent RFG producers from using conventional gasoline as an outlet for undesirable fuel components (anti-dumping requirements). The EPA requirements became effective at the retail level on January 1, 1995.

X3.4.2 The characteristics of reformulated spark-ignition engine fuel, beyond those described by this specification, are described in the research report on reformulated spark-ignition engine fuel.² The research report also includes information on California Air Resources Board Phase 2 gasoline requirements, which are more restrictive than the EPA RFG requirements and take effect at the retail level on June 1, 1996.

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X4. METHOD FOR CALCULATING MASS PERCENT OXYGEN OF GASOLINE-OXYGENATE BLENDS

X4.1 Scope

X4.1.1 Test Method D 4815 provides a procedure for calculating the mass oxygen content of fuels using oxygenate concentration in mass percent. When oxygenate concentration in mass percent is not available, the oxygen concentration of these fuels can be determined indirectly by: (1) measuring the volume concentration of the oxygenates in the blend, which may be reported from Test Method D 4815 or equivalent method (2) measuring the density or relative density of the blend, (3) converting the oxygenate concentrations from volume to mass concentrations, and (4) converting the mass oxygenate concentrations to mass oxygen concentrations using the oxygen mass fractions of the oxygenates present.

X4.2 Procedure

X4.2.1 The following steps are used to determine the total mass oxygen concentration of gasoline-oxygenate blends when indirect calculation is necessary.

X4.2.1.1 Determine the volume concentrations of oxygenates in a gasoline-oxygenate blend (Test Method D 4815 or equivalent test method).

X4.2.1.2 Determine the density or relative density of the gasoline-oxygenate blend (Test Methods D 287, D 1298, or D 4052).

X4.2.1.3 The oxygen mass percent of the gasoline-oxygenate blend is calculated using the following general equation. The densities or relative densities and oxygen mass fractions of a number of pure oxygenates are provided in Table X4.1 for use in Eq (X4.1). The choice of density or relative density must be the same as determined in X4.2.1.2 for the gasoline-oxygenate blend.

Oxygen, Mass % =

$$\frac{V_1 \times d_1 \times O_1 + V_2 \times d_2 \times O_2 + \dots + V_n \times d_n \times O_n}{V_b \times d_b} \times 100 \quad (\text{X4.1})$$

where:

V_n = volume percent of oxygenates 1 through n ,

d_n = density or relative density of oxygenates 1 through n ,

O_n = mass fraction oxygen in oxygenates 1 through n ,

V_b = volume percent of gasoline-oxygenate blend = 100, and

d_b = density or relative density of gasoline-oxygenate blend.

TABLE X4.1 Densities, Relative Densities, and Oxygen Mass Fractions of Pure Oxygenates

Oxygenate	Density, g/mL 20°C (68°F)	Relative Density 15.56/15.56°C (60/60°F)	Oxygen Mass Fraction
Methyl Alcohol	0.7913	0.7963	0.4993
Ethyl Alcohol	0.7894	0.7939	0.3473
n-Propyl Alcohol	0.8038	0.8080	0.2682
Isopropyl Alcohol	0.7855	0.7889	0.2682
n-Butyl Alcohol	0.8097	0.8137	0.2158
Isobutyl Alcohol	0.8016	0.8058	0.2158
sec-Butyl Alcohol	0.8069	0.8114	0.2158
tert-butyl Alcohol	0.7868 ^A	0.7922 ^A	0.2158
Methyl tert-butyl Ether	0.7408	0.7460	0.1815
Ethyl tert-butyl Ether	0.7399	0.7452	0.1588
tert-butyl Methyl Ether	0.7707	0.7758	0.1588
tert-butyl Methyl Ether	0.7815	0.7860	0.1377
Diisopropyl Ether	0.7235	0.7282	0.1586

^A Extrapolated, below freezing temperature.

X4.3 Example Calculation

X4.3.1 Assume that a gasoline-oxygenate blend is reported to contain 9.5 volume percent ethanol and 2.0 volume percent methyl tertiary-butyl ether and that the relative density of the blend is measured to be 0.7450, 15.56/15.56°C (60/60°F).

X4.3.2 Using the relative density and oxygen mass fraction data for ethanol and methyl tertiary-butyl ether from Table X4.1, the following mass percent oxygen is calculated for this gasoline-oxygenate blend.

Oxygen, Mass % =

$$\frac{9.5 \times 0.7939 \times 0.3473 + 2.0 \times 0.7460 \times 0.1815}{100 \times 0.7450} \times 100$$

$$= 3.88$$

X4.4 Precision

X4.4.1 The precision of this calculation method is a function of the individual precisions of density or relative density (Test Methods D 287, D 1298, or D 4052) and oxygenate analysis (Test Method D 4815 or equivalent). Because the repeatability and reproducibility vary with the analyses used, no estimate is provided.

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EXHIBIT 4



US005697987A

United States Patent [19]
Paul

[11] **Patent Number:** **5,697,987**
[45] **Date of Patent:** **Dec. 16, 1997**

[54] **ALTERNATIVE FUEL**

[75] **Inventor:** **Stephen F. Paul, Princeton, N.J.**

[73] **Assignee:** **The Trustees of Princeton University,
Princeton, N.J.**

[21] **Appl. No.:** **644,907**

[22] **Filed:** **May 10, 1996**

[51] **Int. Cl.⁶** **C10L 1/18; C10L 1/16**

[52] **U.S. Cl.** **44/352; 44/451**

[58] **Field of Search** **44/350, 352, 446,
44/451**

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[57] **ABSTRACT**

A spark ignition motor fuel composition consisting essentially of: a hydrocarbon component containing one or more hydrocarbons selected from five to eight carbon atoms straight-chained or branched alkanes essentially free of olefins, aromatics, benzene and sulfur, wherein the hydrocarbon component has a minimum anti-knock index of 65 as measured by ASTM D-2699 and D-2700 and a maximum DVPE of 15 psi as measured by ASTM D-5191; a fuel grade alcohol; and a co-solvent for the hydrocarbon component and the fuel grade alcohol; wherein the hydrocarbon component, the fuel grade alcohol and the co-solvent are present in amounts selected to provide a motor fuel with a minimum anti-knock index of 87 as measured by ASTM D-2699 and D-2700, and a maximum DVPE of 15 psi as measured by ASTM D-5191. A method for lowering the vapor pressure of a hydrocarbon-alcohol blend by adding a co-solvent for the hydrocarbon and the alcohol to the blend is also disclosed.

16 Claims, No Drawings

ALTERNATIVE FUEL

BACKGROUND OF THE INVENTION

The present invention relates to spark ignition motor fuel compositions based on liquid hydrocarbons derived from biogenic gases that are blended with a fuel grade alcohol and a co-solvent for the liquid hydrocarbon and the alcohol, and having an anti-knock index, a heat content, and a Dry Vapor Pressure Equivalent (DVPE) effective to fuel a spark ignition internal combustion engine with minor modifications. In particular, the present invention relates to Coal Gas Liquid (CGL) or Natural Gas Liquids (NGL's)-ethanol blends in which the co-solvent is biomass-derived 2-methyltetrahydrofuran (MTHF).

A need exists for alternatives to gasoline motor fuels for spark ignition internal combustion engines. Gasoline is derived from the extracting of crude oil from oil reservoirs. Crude oil is a mixture of hydrocarbons that exist in liquid phase in underground reservoirs and remains liquid at atmospheric pressure. The refining of crude oil to create conventional gasoline involves the distillation and separation of crude oil components, gasoline being the light naptha component.

Only 10 percent of the world reserves of crude oil lie in the United States, with an overwhelming majority of the remaining 90 percent located outside the boundaries, not only of the United States, but also its North American free trade partners. Over 50 percent of conventional gasoline is imported, with this number to increase steadily into the next century.

Conventional gasoline is a complex composite of over 300 chemicals, including naphthas, olefins, alkenes, aromatics and other relatively volatile hydrocarbons, with or without small quantities of additives blended for use in spark ignition engines. The amount of benzene in regular gasoline can range up to 3-5 percent, and the amount of sulfur to 500 ppm. Reformulated gasoline (RFG) limits the quantity of sulfur to 330 ppm and benzene to 1 percent, and limits the levels of other toxic chemicals as well.

Conventional alternatives to crude oil-derived fuels such as compressed natural gas, propane and electricity require large investments in automobile modification and fuel delivery infrastructure, not to mention technological development. A need exists for an alternative fuel that provides the combustion properties of motor gasoline without requiring significant engine modification, and that can be stored and delivered like motor gasoline. In order to be an advantageous alternative for gaseous alternative fuels such as methane and propane, liquid alternative fuels should also meet all Environmental Protection Agency (EPA) requirements for "clean fuels."

CGL and NGL's have unsuitably low anti-knock indexes and have thus been under-utilized as alternatives to crude oil as hydrocarbon sources for spark ignition engine motor fuels. Attempts to overcome this deficiency have rendered these hydrocarbon streams unsuitable for use as alternative fuels.

Coal gases have long been recognized because of explosions that have occurred in the course of coal mining. This gas is considered a hazard to operations and has been vented to insure safe operation. However, such venting contributes to the increasing amounts of atmospheric methane, which is a potent greenhouse gas. C. M. Boyer, et al., *U.S. EPA, Air and Radiation (ANR-445) EPA/400/9-90/008*. Coal gases can contain significant amounts of heavier hydrocarbons, with C₂₊ fractions as high as 70 percent. Rice, *Hydrocar-*

bons from Coal (American Association of Petroleum Geologists, Studies in Geology #38, 1993) p. 159.

In contrast to the sourcing of conventional gasoline, over 70 percent of the world reserves of NGL's lie in North America. Imports of NGL's into the United States constitutes less than 10 percent of domestic production. NGL's are recovered from natural gas, gas processing plants, and in some situations, from natural gas field facilities. NGL's extracted by fractionators are also included within the definition of NGL's. NGL's are defined according to the published specifications of the Gas Processors Association and the American Society for Testing and Materials (ASTM). The components of NGL's are classified according to carbon chain length as follows: ethane, propane, n-butane, isobutane and "pentanes plus."

Pentanes-plus is defined by the Gas Processors Association and the ASTM as including a mixture of hydrocarbons, mostly pentanes and heavier, extracted from natural gas and including isopentane, natural gasoline, and plant condensates. Pentanes-plus are among the lowest value NGL's. While propanes and butanes are sold to the chemical industry, pentanes-plus are typically diverted to low-added-value oil refinery streams to produce gasoline. Part of the reason why pentanes plus are not generally desirable as gasoline is because they have a low anti-knock index that detracts from its performance as a spark ignition engine motor fuel, as well as a high DVPE which would result in engine vapor lock in warm weather. One advantage of pentanes plus over the other NGL's is that it is liquid at room temperature. Therefore is the only component that can be used in useful quantities as a spark ignition engine motor fuel without significant engine or fuel tank modification.

U.S. Pat. No. 5,004,850 discloses an NGL's-based motor fuel for spark ignition engines in which natural gasoline is blended with toluene to provide a motor fuel with satisfactory anti-knock index and vapor pressure. However, toluene is an expensive, crude oil-derived aromatic hydrocarbon. Its use is severely restricted under the reformulated fuel provision of the 1990 Clean Air Act Amendments.

The United States is the world's largest producer of fuel alcohol, with less than 10 percent of ethanol imported. Ethanol is a biomass-derived, octane-increasing motor fuel additive. While ethanol alone has a low vapor pressure, when blended alone with hydrocarbons, the resulting mixture has an unacceptably high rate of evaporation to be used in EPA designated ozone non-attainment areas, which include most major metropolitan areas in the United States. The vapor pressure properties of ethanol do not predominate in a blend with pentanes plus until the ethanol level exceeds 60 percent by volume. However, blends containing such a high level of ethanol are costly and difficult to start in cold weather because of the high heat of vaporization of ethanol. Furthermore, ethanol has a low heat content, resulting in low fuel economy compared to gasoline.

Low-cost production of MTHF and the production and use of biomass-derived materials such as ethanol or MTHF as gasoline extenders at levels up to about 10 percent by volume is disclosed by Wallington et al., *Environ. Sci. Technol.*, 24, 1596-99 (1990); Rudolph et al., *Biomass*, 16, 33-49 (1988); and Lucas et al., *SAE Technical Paper Series*, No. 932675 (1993). Low-cost production of MTHF and its suitability as a low-octane oxygenate for addition to gasoline with or without ethanol to produce an oxygenated motor fuel was disclosed in an unpublished presentation to the Governors' Ethanol Coalition by Stephen W. Fitzpatrick, Ph.D., of Biofine, Inc. on Feb. 16, 1995. Accurate technical data

involving the blending DVPE and blending octane values for MTHF were not available. There remains a need for a motor fuel having a DVPE and anti-knock index suitable for use in a spark ignition internal combustion engine without significant modification obtained from non-crude oil sources.

SUMMARY OF THE INVENTION

This need is met by the present invention. Co-solvents for CGL, and for NGL's hydrocarbons such as natural gasoline or pentanes plus, and motor fuel alcohols such as ethanol have been discovered that result in a blend having the requisite DVPE and anti-knock index for use in a conventional spark ignition engine with minor modifications.

Therefore, in accordance with the present invention, a spark ignition motor fuel composition is provided consisting essentially of:

a hydrocarbon component consisting essentially of one or more hydrocarbons selected from five to eight carbon atom straight-chained or branched alkanes essentially free of olefins, aromatics, benzene and sulfur, wherein the hydrocarbon component has a minimum anti-knock index of 65 as measured by ASTM D-2699 and D-2700 and a maximum DVPE of 15 psi as measured by ASTM D-5191;

a fuel grade alcohol; and

a co-solvent for the hydrocarbon component and the fuel grade alcohol;

wherein the hydrocarbon component, the fuel grade alcohol and the co-solvent are present in amounts selected to provide a motor fuel with a minimum anti-knock index of 87 as measured by ASTM D-2699 and D-2700, and a maximum DVPE of 15 psi as measured by ASTM D-5191.

Motor fuel compositions in accordance with the present invention may optionally contain n-butane in an amount effective to provide the blend with a DVPE between about 12 and about 15 psi as measured by ASTM D-5191. The n-butane is preferably obtained from NGL's and CGL.

Another embodiment of the present invention provides a method for lowering the vapor pressure of a hydrocarbon-alcohol blend. Methods in accordance with this embodiment of the present invention blend a motor fuel grade alcohol and one or more hydrocarbons obtained from Natural Gas Liquids with an amount of a co-solvent for the alcohol and the hydrocarbons so that a ternary blend is obtained having a DVPE as measured by ASTM D-5191 lower than the DVPE for a binary blend of the alcohol and the hydrocarbons.

The co-solvent for the hydrocarbon component and the fuel grade alcohol in both the fuel compositions and methods of the present invention is preferably derived from waste cellulosic biomass materials such as corn husks, corn cobs, straw, oat/rice hulls, sugar cane stocks, low-grade waste paper, paper mill waste sludge, wood wastes, and the like. Co-solvents capable of being derived from waste cellulosic matter include MTHF and other heterocyclic ethers such as pyrans and oxepans. MTHF is particularly preferred because it can be produced in high yield at low cost with bulk availability, and possesses the requisite miscibility with hydrocarbons and alcohols, boiling point, flash point and density.

Fuel compositions in accordance with the present invention thus may be derived primarily from renewable, domestically-produced, low cost waste biomass materials such as ethanol and MTHF in combination with hydrocarbon condensates otherwise considered extraction losses of

domestic natural gas production such as pentanes plus, and are substantially free of crude oil derivatives. The compositions are clean alternative fuels that contain no olefins, aromatics, heavy hydrocarbons, benzene, sulfur, or any products derived from crude oil. The compositions emit fewer hydrocarbons than gasoline, to help states reduce ozone and meet federal ambient air quality standards. Compositions may be prepared that meet all EPA requirements for "clean fuels," yet at the same time utilize current automobile technology with only minor engine modifications. The compositions require little more than presently existing fuel delivery infrastructure and are based on components that result in a blend that is capable of being competitively priced with gasoline. Other features of the present invention will be pointed out in the following description and claims, which disclose the principles of the invention and the best modes which are presently contemplated for carrying them out.

The above and other features and advantages of the present invention will become clear from the following description of the preferred embodiments considered in conjunction with the accompanying drawings.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

The compositions of the present invention are virtually free of undesirable olefins, aromatics, heavy hydrocarbons, benzene and sulfur, making the fuel compositions very clean burning. The fuel compositions of the present invention may be utilized to fuel conventional spark-ignition internal combustion engines with minor modification. The primary requirement is the lowering of the air/fuel ratio to between about 12 and about 13, as opposed to 14.6, typical of gasoline fueled engines. This adjustment is necessary because of the large quantity of oxygen that is already contained in the fuel.

This adjustment can be accomplished in vehicles manufactured in 1996 and thereafter by software modifications to the on-board engine computer. For older cars, it will be necessary to replace a chip in the on-board engine computer, or, in some cases, to replace the on-board engine computer entirely. Carbureted vehicles, on the other hand, can be readily adjusted to the appropriate air/fuel ratio, and at most will require a simple orifice replacement. Vehicles fueled by the compositions of the present invention preferably should be adapted to run on ethanol or methanol by having fuel system components installed that are compatible with ethanol and methanol, and do not have parts in contact with the fuel made from ethanol and methanol sensitive materials such as nitrile rubber, and the like.

The Clean Air Act Amendments of 1990 set maximum values for both olefins and aromatics, because they result in emission of unburned hydrocarbons. A maximum of 24.6 percent by volume of aromatics may be present in the winter, and 32.0 percent by volume in the summer. A maximum of 11.9 percent by volume of olefins may be present in the winter, and a maximum of 9.2 percent by volume in the summer. Benzene must be present at a level less than or equal to 1.0 percent by volume, and the maximum permitted sulfur is 338 ppm. The fuel compositions of the present invention are essentially free of such materials.

Motor fuel compositions according to the invention are produced by blending one or more hydrocarbons with a fuel grade alcohol selected from methanol, ethanol and mixtures thereof and a co-solvent for the one or more hydrocarbons and the fuel grade alcohol. The fuel grade alcohol is added

to increase the anti-knock index of the hydrocarbon component. The co-solvents of the present invention make it possible to add to the motor fuel compositions significant quantities of alcohol effective to provide an acceptable combination of anti-knock index and DVPE. Suitable fuel grade alcohols can be readily identified and obtained for use in the present invention by one of ordinary skill in the art.

Other anti-knock index increasing additives may be used as well, including those additives, such as toluene, derived from crude oil. However, preferred compositions in accordance with the present invention will be substantially free of crude oil derivatives, including crude oil-derived additives for increasing the anti-knock index.

Essentially any hydrocarbon source containing one or more 5 to 8 carbon atom straight-chained or branched alkanes is suitable for use with the present invention if the hydrocarbon source, as a whole, has a minimum anti-knock index of 65 as measured by ASTM D-2699 and D-2700 and a maximum DVPE of 15 psi as measured by ASTM D-5191. Those of ordinary skill in the art understand the term "anti-knock index" to refer to the average of the Research Octane No. as measured by ASTM D-2699 and the Motor Octane No. as measured by ASTM D-2700. This is commonly expressed as (R+M)/2.

The hydrocarbon component is preferably derived from CGL or NGL's, and is more preferably the NGL's fraction defined by the Gas Processors Association and the ASTM as pentanes plus, which is a commercially available commodity. However, any other hydrocarbon blend having an equivalent energy content, oxygen content and combustion properties may also be used. For example, the fraction of NGL's defined by the Gas Processors Association and the ASTM as "natural gasoline" can be blended with isopentane and substituted for pentanes plus. Natural gasoline alone may be used, as well. In most circumstances, the preparation of blends instead of using "straight" pentanes plus or natural gasoline will be more costly. While any other equivalent blend may be used, similar cost considerations apply.

The hydrocarbon component is blended with the fuel grade alcohol using a co-solvent selected to provide a blend with a DVPE below 15 psi without a sacrifice in the anti-knock index or flash point of the resulting blend, so that a motor fuel composition is obtained suitable for use in a spark ignition engine with minor modifications. Co-solvents suitable for use with the present invention are miscible in both the hydrocarbons and the fuel grade alcohol and have a boiling point high enough to provide a DVPE less than 15 psi in the final blend, preferably greater than 75° C. The co-solvent should have a flash point low enough to ensure cold starting of the final blend, preferably less than -10° C. The co-solvent should also have at least an 85° C. difference between the boiling point and flash point and a specific gravity greater than 0.78.

Five to seven atom heterocyclic ring compounds are preferred as the co-solvent. The heteroatomic polar ring structure is compatible with fuel grade alcohols, yet possesses non-polar regions compatible with hydrocarbons. The heteroatomic structure also functions to depress the vapor pressure of the co-solvent and consequently the resulting blend. The same advantageous properties can also be obtained from short-chained ethers; however, ring compounds are preferred.

Saturated alkyl-branched heterocyclic compounds with a single oxygen atom in the ring are preferred, because the alkyl branching further depresses the vapor pressure of the co-solvent. The ring compound may contain multiple alkyl

branches however, a single branch is preferred. MTHF is an example of a five-membered heterocyclic ring with one methyl branch adjacent to the oxygen atom in the ring.

While nitrogen containing ring compounds are included among the co-solvents of the present invention, they are less preferred because the nitrogen heteroatoms form oxides of nitrogen combustion products, which are pollutants. Thus, oxygen-containing heterocyclic ring compounds are preferred over rings with nitrogen heteroatoms, with alkylated ring compounds being more preferred. In addition, the ring oxygen also functions as an oxygenate that promotes cleaner burning of the motor fuel compositions of the present invention. Thus, oxygen-containing heterocyclic ring compounds are particularly preferred co-solvents in the motor fuel compositions of the present invention because of their ability as oxygenates to provide a cleaner burning fuel composition which is in addition to their being a vapor pressure-lowering co-solvent for hydrocarbons and fuel grade alcohols.

Accordingly, oxygen-containing saturated five- to seven atom heterocyclic rings are most preferred. MTHF is particularly preferred. While MTHF is considered an octane depressant for gasoline, it improves the octane rating of NGL's. Not only does MTHF have superior miscibility with hydrocarbons and alcohols and a desirable boiling point, flash point and density, MTHF is a readily available, inexpensive, bulk commodity item. MTHF also has a higher heat content than fuel grade alcohols and does not pick up water as alcohols do, and is thus fungible in an oil pipeline. This permits larger quantities of the fuel grade alcohols to be used to increase the anti-knock index of the motor fuel compositions.

In addition, MTHF is commercially derived from the production of levulinic acid from waste cellulosic biomass such as corn husks, corn cobs, straw, oat/flee hubs, sugar cane stocks, low-grade waste paper, paper mill waste sludge, wood wastes, and the like. The production of MTHF from such cellulosic waste products is disclosed in U.S. Pat. No. 4,897,497. MTHF that has been produced from waste cellulosic biomass is particularly preferred as a co-solvent in the motor fuel compositions of the present invention.

Examples of other suitable co-solvents, selected on the basis of boiling point, flash point, density and miscibility with fuel grade alcohols and pentanes plus, are 2-methyl-2-propanol, 2-buten-2-one, tetrahydropyran, 2-ethyltetrahydrofuran (ETHF), 3,4-dihydro-2H-pyran, 3,3-dimethyloxetane, 2-methylbutyraldehyde, butylethyl ether, 3-methyltetrahydropyran, 4-methyl-2-pentanone, diallyl ether, allyl propyl ether, and the like. As is readily apparent from the above list, short-chained ethers function as well as heterocyclic ring compounds with respect to miscibility with hydrocarbons and fuel grade alcohols and vapor pressure depression of the resulting motor fuel composition. Like the oxygen-containing heterocyclic ring compounds, short-chained ethers are also ideally vapor pressure-lowering oxygenates.

The motor fuel compositions of the present invention optionally include n-butane in an amount effective to provide a DVPE between about 7 and about 15 psi. However, the compositions may be formulated to provide a DVPE as low as 3.5 psi. The higher DVPE is desirable in the northern United States and Europe during winter to promote cold weather starting. Preferably, the n-butane is obtained from NGL's or CGL.

The motor fuel compositions also optionally include conventional additives for spark ignition motor fuels. Thus,

the motor fuel compositions of the present invention may include conventional amounts of detergent, anti-foaming, and anti-icing additives and the like. The additives may be derived from crude oil; however, preferred compositions in accordance with the present invention are substantially free of crude oil derivatives.

The motor fuel compositions of the present invention are prepared using conventional rack-blending techniques for ethanol-containing motor fuels. Preferably, to prevent evaporative loss emissions, the dense co-solvent component is first pumped cold (less than 70° F.) through a port in the bottom of a blending tank. The hydrocarbons are then pumped without agitating through the same port in the bottom of the tank to minimize evaporative loss. If used, n-butane is pumped cold (less than 40° F.) through the bottom of the tank. The butane is pumped next through the bottom port, so it is immediately diluted so that surface vapor pressure is minimized to prevent evaporative losses. Alternatively, two or more of the MTHF, hydrocarbons and n-butane, if used, may be pumped through the bottom port together. If not blended at the distribution rack, the two or three components may be obtained as a blend through conventional gasoline pipelines. Because ethanol alone would otherwise raise the vapor pressure of the hydrocarbons and promote evaporative loss, the ethanol is preferably blended last, after the MTHF and n-butane, if present, has already blended with the hydrocarbon, by conventional splash blending techniques for the introduction of ethanol to motor fuels.

Thus, for a blend containing n-butane, ethanol, MTHF and pentanes plus, the MTHF is first pumped into the blending tank. Without agitation, pentanes-plus is pumped through the bottom of the tank into the MTHF, followed by the n-butane (if used). Finally, ethanol is blended through the bottom. The blend is then recovered and stored by conventional means.

The hydrocarbons, fuel grade alcohol and co-solvent are added in amounts selected to provide a motor fuel composition with a minimum anti-knock index of 87 as measured by ASTM D-2699 and D-2700 and a maximum DVPE of 15 psi as measured by ASTM D-5191. A minimum anti-knock index of 89.0 is preferred, and a minimum anti-knock index of 92.5 is even more preferred. In the summer, a maximum DVPE of 8.1 psi is preferred, with a maximum DVPE of 7.2 psi being more preferred. In the winter, the DVPE should be as close as possible to 15 psi, preferably between about 12 and about 15 psi. For this reason, n-butane may be added to the motor fuel compositions of the present invention in an amount effective to provide a DVPE within this range.

In preferred motor fuel compositions in accordance with the present invention, the hydrocarbon component consists essentially of one or more hydrocarbons obtained from NGL's, blended with ethanol, MTHF and, optionally, n-butane. The NGL's hydrocarbons may be present at a level between about 10 and about 50 percent by volume, the ethanol may be present in an amount between about 25 and about 55 percent by volume, the MTHF may be present in an amount between about 15 and about 55 percent by volume, and the n-butane may be present in a level between zero and about 15 percent by volume. More preferred motor fuel compositions contain from about 25 to about 40 percent by volume of pentanes plus, from about 25 to about 40 percent by volume of ethanol, from about 20 to about 30 percent by volume of MTHF and from zero to about 10 percent by volume of n-butane.

The compositions of the present invention may be formulated as summer and winter fuel blends having T10 and

T90 values as measured by ASTM-D86 within ASTM specifications for summer and winter fuel blends. The winter blend compositions of the present invention are significantly more volatile than conventional gasoline to aid cold weather starting. The T90 values indicate the amount of "heavy-end" components in the fuel. These substances are considered to be a primary source of unburned hydrocarbons during the cold start phase of engine operation. The lower values of "heavy-end" components in the compositions of the present invention also indicates superior emissions performance. The amount of solid residue after combustion is only one-fifth that typically found in conventional gasoline.

A particularly preferred summer fuel blend contains about 32.5 percent by volume of pentanes plus, about 35 percent by volume of ethanol, and about 32.5 percent by volume of MTHF. This blend is characterized as follows:

TEST	METHOD	RESULT	CONDI- TIONS
API Gravity	ASTM D4052	52.1	60° F.
Distillation	ASTM D86		
Initial Boiling Point		107.0° C.	
T10		133.2° F.	
T50		161.8° F.	
T90		166.9° F.	
Final Boiling Point		195.5° F.	
Recovered		99.5 wt. %	
Residue		0.3 wt. %	
Loss		0.2 wt. %	
DVPE	ASTM D5191	8.10 psi	
Lead	ASTM D3237	<0.01 g/gal	
Research Octane No.	ASTM D2699	96.8	
Motor Octane No.	ASTM D2700	82.6	
R + M/2	ASTM D4814	89.7	
(Anti-Knock Index)			
Copper Corrosion	ASTM D130	1A	3 hrs. @ 122° F.
Gum, (After Wash)	ASTM D381	2.2 mg/100 mL	
Sulfur	ASTM D2622	3.0 ppm	
Phosphorous	ASTM D3231	<0.004 g/gal	
Oxidation Stability	ASTM D525	165 min	
Oxygenates	ASTM D4815		
Ethanol		34.87 vol %	
Oxygen	ASTM D4815	18.92 wt %	
Benzene	ASTM D3606	0.15 vol %	
V/L 20	CALCULATED	135° F.	
Doctor Test	ASTM D4952	POSITIVE	
Aromatics	ASTM D1319	.41 vol %	
Olefins	ASTM D1319	0.09 vol %	
Mercaptan Sulfur	ASTM D3227	.0010 wt %	
Water Tolerance	ASTM D4814	<-65° C.	
Heat Content	ASTM D3338	18,663 BTU/lb	

A particularly preferred winter fuel blend contains about 40 percent by volume of pentanes plus, about 25 percent by volume of ethanol, about 25 percent by volume of MTHF and about 10 percent by volume of n-butane. This blend is characterized as follows:

TEST	METHOD	RESULT	CONDI- TIONS
API Gravity	ASTM D4052	59.0	60° F.
Distillation	ASTM D86		
Initial Boiling Point		83.7° F.	
T10		102.7° F.	
T50		154.1° F.	
T90		166.5° F.	
Final Boiling Point		235.6° F.	
Recovery		97.1 wt. %	
Residue		1.2 wt. %	
Loss		2.9 wt. %	

-continued

TEST	METHOD	RESULT	CONDI- TIONS
DVPE	ASTM D5191	14.69 psi	
Lead	ASTM D3237	<0.01 g/gal	
Research Octane No.	ASTM D2699	93.5	
Motor Octane No.	ASTM D2700	84.4	
R + M/2	ASTM D4814	89.0	
(Anti-Knock Index)			
Copper Corrosion	ASTM D130	1A	3 hrs. @ 122° F.
Gum, (After Wash)	ASTM D381	<1 mg/100 mL	
Sulfur	ASTM D2622	123 ppm	
Phosphorous	ASTM D3231	<0.004 g/gal	
Oxidation Stability	ASTM D525	105 min	
Oxygenates	ASTM D4815		
Ethanol		25.0 vol %	
Oxygen	ASTM D4815/ OFID	9.28 wt %	
Benzene	ASTM D3606	0.18 vol %	
V/L 20	CALCULATED	101° F.	
Doctor Test	ASTM D4952	POSITIVE	
Aromatics GC-MSD		0.51 vol %	
Olefins	ASTM D1319	2.6 vol %	
Mercaptan Sulfur	ASTM D3227		
Water Tolerance	ASTM D4814	<-65° C.	
Heat Content	ASTM D3338	18,776 BTU/lb	

A preferred summer premium blend contains about 27.5 percent by volume of pentanes plus, about 55 percent by volume of ethanol and about 17.5 percent by volume of MTHF. The blend is characterized as follows:

TEST	METHOD	RESULT	CONDI- TIONS
API Gravity	ASTM D4052	58.9	60° F.
Distillation	ASTM D86		
Initial Boiling Point		103.5° F.	
T10		128.2° F.	
T50		163.7° F.	
T90		169.8° F.	
Final Boiling Point		175.0° F.	
Recovered		99.0 wt. %	
Residue		0.6 wt. %	
Loss		0.4 wt. %	
DVPE	ASTM D5191	8.05 psi	
Lead	ASTM D3237	<0.01 g/gal	
Research Octane No.	ASTM D2699	100.5	
Motor Octane No.	ASTM D2700	85.4	
R + M/2	ASTM D4814	93.0	
(Anti-Knock Index)			
Copper Corrosion	ASTM D130	1A	3 hrs. @ 122° F.
Gum, (After Wash)	ASTM D381	1.6 mg/100 mL	
Sulfur	ASTM D2622	24 ppm	
Phosphorous	ASTM D 3231	<0.004 g/gal	
Oxidation Stability	ASTM D525	150 min	
Oxygenates	ASTM D4815		
Ethanol		54.96 vol %	
Oxygen	ASTM D4815	19.98 wt %	
Benzene	ASTM D3606	0.22 vol %	
V/L 20	CALCULATED	126° F.	
Doctor Test	ASTM D4952	POSITIVE	
Aromatics	ASTM D1319	0.20 vol %	
Olefins	ASTM D1319	0.15 vol %	
Mercaptan Sulfur	ASTM D3227	.0008 wt %	
Water Tolerance	ASTM D4814	<-65° C.	
Heat Content	ASTM D3338	18,793 BTU/lb	

A preferred winter premium blend contains about 16 percent by volume of pentanes plus, about 47 percent by volume of ethanol, about 26 percent by volume of MTHF and about 11 percent by volume of n-butane. The blend is characterized as follows:

TEST	METHOD	RESULT	CONDI- TIONS
5 API Gravity	ASTM D4052	51.6	60° F.
Distillation	ASTM D86		
Initial Boiling Point		83.7° F.	
T10		109.7° F.	
T50		165.2° F.	
T90		168.7° F.	
Final Boiling Point		173.4° F.	
10 Recovery		97.9 wt. %	
Residue			
Loss		2.1 wt. %	
DVPE	ASTM D5191	14.61 psi	
Lead	ASTM D3237	<0.01 g/gal	
15 Research Octane No.	ASTM D2699	101.2	
Motor Octane No.	ASTM D2700	85.4	
R + M/2	ASTM D4814	93.3	
(Anti-Knock Index)			
Copper Corrosion	ASTM D130	1A	3 hrs. @ 122° F.
Gum, (After Wash)	ASTM D381	<1 mg/100 mL	
20 Sulfur	ASTM D2622	111 ppm	
Phosphorous	ASTM D3231	<0.004 g/gal	
Oxidation Stability	ASTM D525	210 min	
Oxygenates	ASTM D4815		
Ethanol		47.0 vol %	
Oxygen	ASTM D4815/ OFID	16.77 wt %	
25 Benzene	ASTM D3606	0.04 vol %	
V/L 20	CALCULATED		
Doctor Test	ASTM D4952	POSITIVE	
Aromatics	GC-MSD	0.17 vol %	
Olefins	ASTM D1319	0.85 vol %	
30 Mercaptan Sulfur	ASTM D3227		
Water Tolerance	ASTM D4814	<-65° C.	
Heat Content	ASTM D3338	18,673 BTU/lb	

Thus, it will be appreciated that the present invention provides a motor gasoline alternative essentially free of crude oil products that can fuel a spark ignition internal combustion engine with minor modifications, yet can be blended to limit emissions resulting from evaporative losses. The present invention provides fuel compositions containing less than 0.1 percent benzene, less than 0.5 percent aromatics, less than 0.1 percent olefins and less than 10 ppm sulfur. The following examples further illustrate the present invention, and are not to be construed as limiting the scope thereof. All parts and percentages are by volume unless expressly indicated to be otherwise and all temperatures are in degrees Fahrenheit.

EXAMPLE I

A fuel composition in accordance with the present invention was prepared by blending 40 percent by volume of natural gasoline procured from Daylight Engineering, Elberfield, Ind., 40 percent by volume of 200 proof ethanol procured from Pharmco Products, Inc., Brookfield, Conn., and 20 percent by volume of MTHF purchased from the Quaker Oats Chemical Company, West Lafayette, Ind. 2 liters of ethanol was pre-blended with 1 liter of MTHF in order to avoid evaporative loss of the ethanol upon contact with the natural gasoline. The ethanol and MTHF were cooled to 40° F. prior to blending to further minimize evaporative losses.

2 liters of the natural gasoline was added to a mixing tank. The natural gasoline was also cooled to 40° F. to minimize evaporative losses. The blend of ethanol and MTHF was then added to the natural gasoline with mixing. The mixture was gently stirred for 5 seconds until a uniform, homogeneous blend was obtained.

The content of the natural gasoline was analyzed by Incheape Testing Services (Caleb-Brett) of Linden, N.J. It

was found to consist of the following components:

Butane	Not Found
Isopentane	33 Vol. %
n-Pentane	21 Vol. %
Isobutane	26 Vol. %
n-Hexane	11 Vol. %
Isobutane	6 Vol. %
n-Heptane	2 Vol. %
Benzene	<1 Vol. %
Toluene	<0.5 Vol. %

Thus, while Daylight Engineering refers to this product as "natural gasoline," the product conforms to the Gas Processor's Association's definition of pentanes plus, as well as the definition of pentanes plus for purposes of the present invention.

The motor fuel was tested on a 1984 Chevrolet Caprice Classic with a 350 CID V-8 engine and a four barrel carburetor (VIN 1G1AN69H4EX149195). A carbureted engine was chosen so that adjustment of the idle fuel mixture was possible without electronic intervention. There was a degree of electronic fuel management in that the oxygen content in the exhaust, manifold air pressure, throttle position and coolant temperature were measured. Pollution tests were performed at two throttle positions, fast-idle (1950 rpm) and slow-idle (720 rpm). THC (total hydrocarbons), CO (carbon monoxide), O₂ and CO₂ exhaust emissions were recorded with a wand-type four-gas analyzer.

The engine was examined and a broken vacuum line was replaced. The idle-speed and spark timing were adjusted to manufacturer's specifications. The ignition "spark line" appeared to be even, indicating no undue problem with any of the spark plugs or wires. The manifold vacuum was between 20 and 21 inches and steady, indicating no difficulties with the piston rings or intake and exhaust valves.

At the time this test was performed in the New York Metropolitan area, conventional gasoline was not available at retail. Therefore, the comparison was not made with a "base line gasoline" as defined in the Clean Air Act, but with a fuel already formulated to burn more cleanly. The emissions tests performed on the above fuel composition were compared to SUNOCO 87-octane reformulated gasoline purchased at a retail service station. Tests were performed on the same engine, on the same day, and within one hour of each other. The three tests included: (1) fast and slow idle emissions tests for total hydrocarbons (THC) and carbon monoxide (CO), (2) fast-idle fuel consumption, and (3) 2.7 mile road test for fuel economy and driveability. The summary of the emissions tests is shown in the following table:

Time Of Day	Idle Speed (rpm)	Fuel	THC (ppm)	CO (%)
09:46	720	Sunoco-87	132	0.38
09:54	720	Sunoco-87	101	0.27
09:55	1950	Sunoco-87	132	0.61
10:42	700	NGL's/ethanol	76	0.03
10:44	720	NGL's/ethanol	65	0.02
10:48	1900	NGL's/ethanol	98	0.01

It should be noted that the New Jersey state emissions requirements for model years 1981 to the present are THC<220 ppm and CO<1.2 percent.

The engines were operated at fast idle (1970 rpm) for approximately 7 minutes. Fuel consumption for the above

fuel composition was 650 mL in 6 minutes and 30 seconds (100 mL per minute). The fuel consumption for the reformulated gasoline was 600 mL in 7 minutes (86 mL per minute). The 2.7 mile on-road test showed no significant difference in fuel consumption (900 mL for the above fuel composition and 870 mL for the reformulated gasoline).

Compared with the reformulated gasoline, the above fuel composition reduced CO emissions by a factor of 10, and THC emissions decreased by 43 percent. In the fast-idle test, the consumption of the above fuel composition was 14 percent greater than the reformulated gasoline. No significant difference in driveability was noticed during the on-road test. During full-throttle acceleration, engine knock was slightly more noticeable with the reformulated gasoline.

Thus, it will be appreciated that the fuel compositions of the present invention can be used to fuel spark-ignited internal combustion engines. The CO and THC emission properties are better than gasoline reformulated to burn cleaner than baseline gasoline, with no significant difference in fuel consumption.

EXAMPLE II

A summer fuel blend was prepared as in Example I, containing 32.5 percent by volume of natural gasoline (Daylight Engineering), 35 percent by volume of ethanol and 32.5 percent by volume of MTHF. A winter fuel blend was prepared as in Example I, containing 40 percent by volume of pentanes plus, 25 percent by volume of ethanol, 25 percent by volume of MTHF and 10 percent by volume of n-butane. The motor fuels were tested along with E₈₅ (E85), a prior art alternative fuel containing 80 percent by volume of 200 proof pure ethyl alcohol and 20 percent by volume of indolene, an EPA certification test fuel defined in 40 C.F.R. § 86 and obtained from Sunoco of Marcus Hook, Pa. The E85 was prepared according to the method disclosed in Example I. The three fuels were tested against indolene as a control on a 1996 Ford Taurus GL sedan ethanol Flexible Fuel Vehicle (VIN 1FALT522XSG195580) with a fully warmed-up engine. Emissions testing was performed at Compliance and Research Services, Inc. of Linden, N.J.

The vehicle was loaded on a Clayton Industries, Inc., Model ECE-50 (split roll) dynamometer. The dynamometer was set for an inertial test weight of 3,750 lbs. The exhaust gases were sampled with a Horiba Instruments, Inc. Model CVS-40 gas analyzer. Hydrocarbons (THC) were analyzed with a Horiba Model FIA-23A Flame Ionization Detector (FID). Carbon Monoxide (CO) and Carbon Dioxide (CO₂) were analyzed with a Horiba Model AIA-23 Non-Dispersive Infrared Detector (NDIR). Hydrocarbon speciation was performed on a Gas Chromatograph with a FID manufactured by Perkin Elmer Inc. The GC column was a Supelco 100Mx0.25 mmx0.50 micron Petrocol DH. All emissions testing equipment was manufactured in 1984.

The summary of emissions sampled directly from the exhaust manifold (before the catalytic converter) are shown in the following table as the percentage reduction of THC and CO for each fuel blend relative to indolene:

ENGINE	SPEED	MPH	WINTER		SUMMER		E85	
			THC	CO	THC	CO	THC	CO
1500	30		-27 ± 23	n.s.	-45 ± 25	n.s.	-42 ± 23	n.s.
2000	41		-35 ± 23	n.s.	-47 ± 31	n.s.	-45 ± 29	n.s.
2500	51		-37 ± 10	n.s.	-53 ± 11	n.s.	-43 ± 11	n.s.
3000	61		-65 ± 18	-71 ± 18	-68 ± 14	-73 ± 13	-50 ± 20	-48 ± 23
3500	67		-71 ± 21	-71 ± 46	-74 ± 21	-76 ± 47	-54 ± 18	-46 ± 41

n.s. = no significant variation

The fuel compositions burned essentially the same as indolene at lower engine rpm's, but significantly better at rpm's of 2500 and greater. In most cases the fuels burned as clean as or cleaner than E85.

The essential feature of the Ford Taurus Flexible Fuel Vehicle was its ability to choose the proper air/fuel ratio for any mixture of fuels used. The vehicle was not modified externally in any way between tests. The Electronic Emissions Computer and fuel sensor showed that the selected air/fuel ratio was as follows:

indolene	14.6
winter blend	12.5
summer blend	11.9
E85	10.4

The foregoing examples and description of the preferred embodiment should be taken as illustrating, rather than as limiting, the present invention as defined by the claims. As will be readily appreciated, numerous variations and combinations of the features set forth above can be utilized without departing from the present invention as set forth in the claims. All such modifications are intended to be included within the scope of the following claims.

What is claimed is:

1. A spark ignition motor fuel composition consisting essentially of:

a hydrocarbon component consisting essentially of a mixture of five to seven carbon atom straight-chained or branched alkanes essentially free of olefins, aromatics and sulfur present in an amount between about 10 and about 50 percent by volume of said motor fuel composition, wherein said hydrocarbon component has a minimum anti-knock index of 65 as measured by ASTM D-2699 and D-2700 and a maximum Dry Vapor Pressure Equivalent of 15 psi as measured by ASTM D-5191, and optionally including n-butane in an amount up to about 15 percent by volume of said motor fuel composition;

ethanol, present in an amount between about 25 and about 55 percent by volume of said motor fuel composition; and

2-methyltetrahydrofuran, present in an amount between about 15 and about 55 percent by volume of said motor fuel composition.

2. The spark ignition motor fuel composition of claim 1, consisting essentially of:

from about 25 to about 40 percent by volume of said hydrocarbon compound;

from about 25 to about 40 percent by volume of ethanol; from about 20 to about 35 percent by volume of 2-methyltetrahydrofuran; and

optionally including up to about 10 percent by volume of n-butane.

3. The motor fuel composition of claim 2, consisting essentially of about 32.5 percent by volume of said hydrocarbon component, about 35 percent by volume of ethanol and about 32.5 percent by volume of 2-methyltetrahydrofuran, and having a Dry Vapor Pressure Equivalent of about 8.3 psi as measured by ASTM D-5191 and an anti-knock index of about 89.7 as measured by ASTM D-2699 and D-2700.

4. The motor fuel composition of claim 2, consisting essentially of about 40 percent by volume of said hydrocarbon component, about 25 percent by volume of ethanol, about 25 percent by volume of 2-methyltetrahydrofuran and about 10 percent by volume of n-butane, and having a Dry Vapor Pressure Equivalent of about 14.7 psi as measured by ASTM D-5191 and an anti-knock index of about 89.0 as measured by ASTM D-2699 and D-2700.

5. The motor fuel composition of claim 1, consisting essentially of about 27.5 percent by volume of said hydrocarbon component, about 55 percent by volume of ethanol and about 17.5 percent by volume of 2-methyltetrahydrofuran, and having a Dry Vapor Pressure Equivalent of about 8.0 psi as measured by ASTM D-5191 and an anti-knock index of about 93.0 as measured by ASTM D-2699 and D-2700.

6. The motor fuel composition of claim 1, consisting essentially of about 16 percent by volume of said hydrocarbon component, about 47 percent by volume of ethanol, about 26 percent by volume of 2-methyltetrahydrofuran and about 11 percent by volume of n-butane, and having a Dry Vapor Pressure Equivalent of about 14.6 psi as measured by ASTM D-5191 and an anti-knock index of about 93.3 as measured by ASTM D-2699 and D-2700.

7. The motor fuel composition of claim 1, consisting essentially of about 40 percent by volume of said hydrocarbon component, about 40 percent by volume of ethanol and about 20 percent by volume of 2-methyltetrahydrofuran.

8. The motor fuel composition of claim 7, wherein said hydrocarbon component, said ethanol and said 2-methyltetrahydrofuran are present in amounts effective to provide a motor fuel with a minimum anti-knock index of 89.0 as measured by ASTM D-2699 and ASTM D-2700.

9. The motor fuel composition of claim 8, wherein said hydrocarbon component, said ethanol and said 2-methyltetrahydrofuran are present in amounts effective to provide a motor fuel with a minimum anti-knock index of 92.5 as measured by ASTM D-2699 and ASTM D-2700.

10. The motor fuel composition of claim 1, wherein said hydrocarbon compound, said ethanol and said 2-methyltetrahydrofuran are present in amounts effective to provide a motor fuel with a maximum DVPE of 8.3 psi as measured by ASTM D-5191.

11. The motor fuel composition of claim 1, wherein said hydrocarbon component, said ethanol and said 2-methyltetrahydrofuran are present in amounts effective to provide a motor fuel with a DVPE between about 12 and about 15 psi as measured by ASTM D-5191.

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12. The spark ignition motor fuel of claim 1, wherein said hydrocarbon component is obtained from Natural Gas Liquids.

13. The spark ignition motor fuel of claim 1, wherein said hydrocarbon component comprises pentanes plus.

14. A method for lowering the vapor pressure of a hydrocarbon-ethanol blend comprising blending between about 25 and about 55 percent by volume of ethanol and between about 10 and about 50 percent by volume of a hydrocarbon component consisting essentially of a mixture of five to seven carbon atom straight-chained or branched alkanes essentially free of olefins, aromatics and sulfur, and having a minimum anti-knock index of 65 as measured by ASTM D-2699 and D-2700 and a maximum Dry Vapor Pressure Equivalent of 15 psi as measured by ASTM D-5191, with an amount of 2-methyltetrahydrofuran between about 15 and about 55 percent by volume, so that

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a ternary blend is obtained having a Dry Vapor Pressure Equivalent as measured by ASTM D-5191 lower than the Dry Vapor Pressure Equivalent for a binary blend of said ethanol and said hydrocarbon obtained from Natural Gas Liquids.

15. The method of claim 14, wherein said ethanol, said hydrocarbons and said 2-methyltetrahydrofuran are present in amounts effective to provide a motor fuel with a minimum anti-knock index of 87 as measured by ASTM D-2699 and D-2700, and a maximum Dry Vapor Pressure Equivalent of 15 psi.

16. The method of claim 14, wherein said hydrocarbons and said 2-methyltetrahydrofuran are pre-blended together before being blended with said ethanol.

* * * * *

**UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION**

PATENT NO. : 5,697,987
DATED : December 16, 1997
INVENTOR(S) : Stephen F. Paul

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

On the title page, under "[73] Assignee:" "Princeton" should read --Princeton--.

Column 6, line 36, "oat/flee hubs" should read --oat/rice hulls--.

Column 7, line 5, "flee" should read --free--.

Column 13, line 62 (line 4 of claim 2), "compound" should read --component--.

Column 14, line 48 (line 1 of claim 8), "claim 7" should read --claim 1--.

Column 16, line 4 (next to last line of claim 14), "hydrocarbon" should read --hydrocarbons--.

Signed and Sealed this
Tenth Day of March, 1998



BRUCE LEHMAN

Attest:

Attesting Officer

Commissioner of Patents and Trademarks